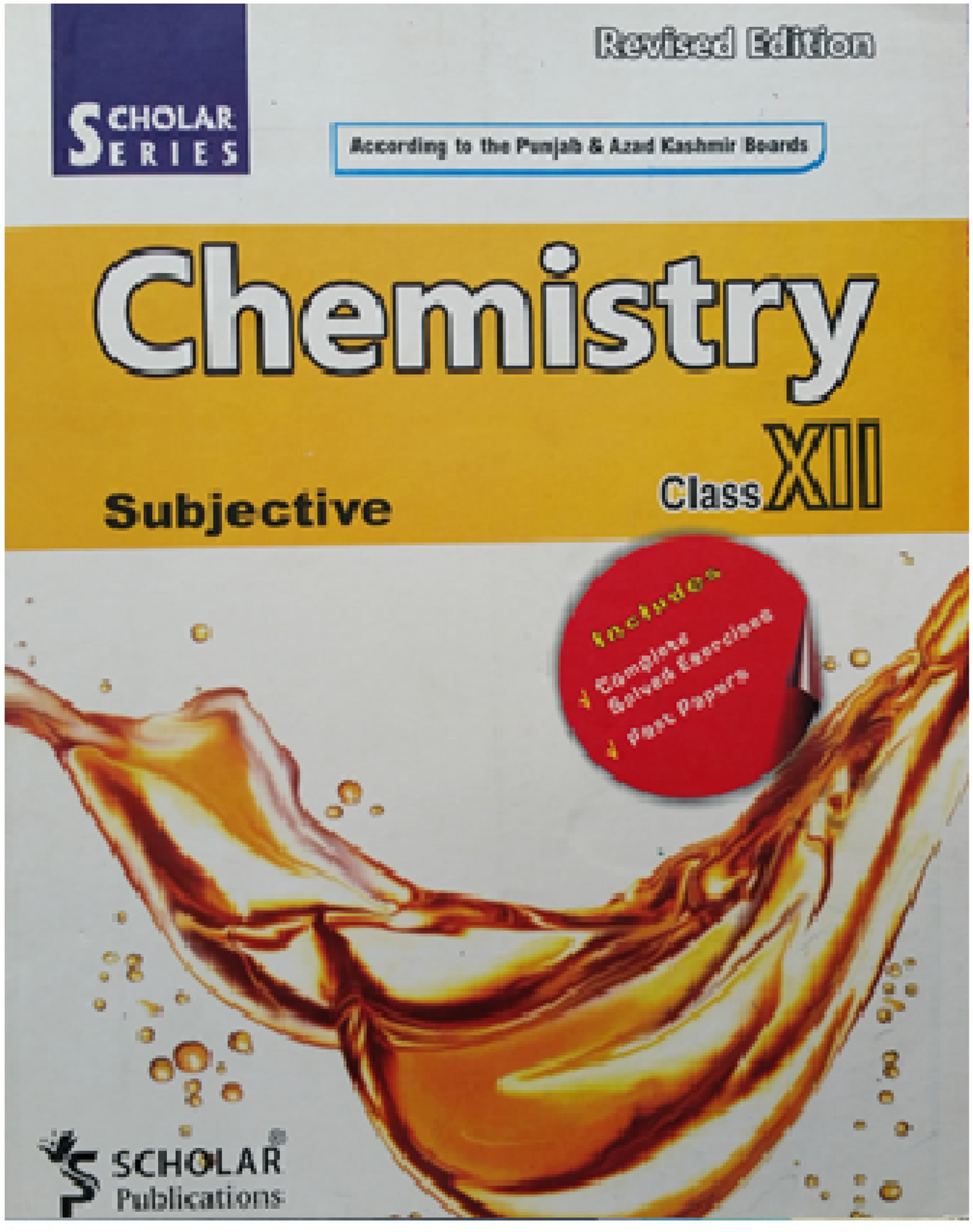


12TH HELPING BOOK PDF

CHAPTER 1

Periodic Classification of Elements and Periodicity

Introduction

To achieve a thorough understanding of a complex subject like chemistry, it would be highly desirable to fit all the facts into a simple logical pattern. The periodic table of elements has served the purpose to systematize the properties of the elements for well over 100 years. The development of periodic table is one of the most significant achievements in the history of chemical sciences.

Periodic table

"A table obtained by the arrangement of elements into periods and groups is called periodic table".

Usefulness of periodic table

The periodic table provides a basic framework to study the periodic behaviour of physical and chemical properties of elements as well as their compounds.

Historical Background

The early history of ideas leading up to the periodic classification of elements is fascinating, but will not be treated here in detail. Those who made memorable contributions in this field are:

Al-Razi

He organized the known elements and compounds. His classification was based upon the physical and chemical properties of elements and compounds.

Dobereiner's Triads

In 1829, a German chemist, Dobereiner arranged then known elements in groups called Triads, as each contained three elements with similar properties. According to his law of Triads:

"The atomic mass of middle element is the average of atomic masses of other two elements of a triad."

Some Dobereiner's Triads

Triad	**Li**	**Na**	**K**	Atomic mass of Na $= \frac{7+39}{2} = 23$
Atomic mass	7	23	39	
Triad	**Ca**	**Sr**	**Ba**	Atomic mass of Sr $= \frac{40+137}{2} = 88.5$
Atomic mass	40	88	137	
Triad	**Cl**	**Br**	**I**	Atomic mass of Br $= \frac{35.5+127}{2} = 81.25$
Atomic mass	35.5	80	127	

Demerits

Dobereiner's idea of classification failed because only a few elements could be covered under triads.

Newland's Law of Octaves

In 1864, an English chemist, John Newland classified 62 elements, known at that time, in increasing order of their atomic masses. According to his law of Octaves:

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"If the elements are arranged in the increasing order of their atomic masses, every eighth (8^{th}) element had some properties in common with the first one."

Newland's Octaves

Li (7)	Be (9)	B (11)	C (12)	N (14)	O (16)	F (19)
Na (23)	Mg (24)	Al (27)	Si (28)	P (31)	S (32)	Cl (35.5)
K (39)	Ca (40)	Ti (48)	Cr (52)	Mn (55)	Fe (56)	Ni & Co

Demerits

(i) It was found that the law of Octaves was applicable only upto calcium, as after calcium every eighth element did not possess properties similar to that of the first.

(ii) It was assumed by Newland that only 62 elements existed in nature and no more elements would be discovered in the future. But, later on, several new elements were discovered, whose properties did not fit into the law of Octaves.

(iii) The above sequence of elements was disturbed with the discovery of noble gases.

Mendeleev's Periodic Table

In 1871, Russian Chemist, Dmitri Mendeleev, gave a more useful and comprehensive scheme for the classification of elements. He presented the first regular periodic table in which elements of similar chemical properties were arranged in eight vertical columns called Groups. The horizontal rows of the table were called Periods and there are 12 Periods in Mendeleev's periodic table.

Mendeleev's Periodic Law

"If the elements are arranged in ascending order of their atomic masses, their chemical properties repeat in a periodic manner."

Significance of Mendeleev's Periodic Table

Some important contributions of Mendeleev's periodic Table are:

- **Systematic study of elements**

  He made the study of 105 elements quite convenient. Knowing the properties of one element in the group, the properties of other elements in the group can be guessed. Thus it becomes very useful in studying and remembering the properties of a large number of elements.

- **Prediction of new elements**

  While arranging elements, he left certain vacant places. These gaps represented the undiscovered elements. Mendeleev predicted the properties of these undiscovered elements on the basis of their positions. For example, he predicted the properties of scandium, gallium and germanium which were discovered later. The observed properties of these elements were found to be similar to those predicted by Mendeleev.

- **Correction of atomic masses**

  The Mendeleev's periodic table helped in correcting the atomic masses of some elements based on their positions in the table. For example, atomic mass of beryllium was corrected from 13.5 to 9. With the help of this table , atomic masses of indium, gold, platinum etc., were corrected.

- **Valency of Elements**

  Mendeleev's classification helped in understanding the valency of elements. The valency of the elements is given by the group number.

Defects in Mendeleev's periodic Table

In spite of its useful role in the study of chemistry, Mendeleev's Table possessed many drawbacks. Some of these drawbacks are:

- **Position of hydrogen:** Hydrogen is placed in Group IA. However, it actually resembles the elements of Group-IA (alkali metals) as well as the elements of Group VII-A (halogens). Thus, the position of hydrogen in the periodic table is not clear.
- **Position of isotopes:** On the basis of atomic weight, various isotopes of the same elements should be assigned different places in the periodic table. Mendeleev could not provide separate places for isotopes.
- **Position of lanthanides and actinides:** Fourteen elements following Lanthanum (known as lanthanides or rare earths) and the fourteen elements following Actinium (known as actinides or transuranic elements) have not been provided separate and proper places in the Mendeleev's table, rather they have been placed in two rows at the bottom of the table.
- **Dissimilar elements placed together:** Noble metals like Cu, Ag and Au are placed along with chemically dissimilar alkali metals in Group I . Similarly, Mn possessing very few similarities with halogens have been placed in VII group.
- **Similar elements separated:** In Mendeleev's periodic table, certain chemically similar elements such as copper and mercury; gold and platinum have been placed in different groups.
- **Anomalous pairs :** In the Mendeleev's Table based on atomic weight, the positions of certain pairs , e.g. Argon(at. wt = 39.94) and potassium (at. wt = 39.1) : Cobalt(at wt =58.93) and nickel (atomic weight = 58.71): Tellurium (atomic weight = 127.60) and iodine (atomic weight = 126.90) would be reversed. In other words, certain pairs of elements are misfit in the periodic table, if atomic weight is the basis of classification.

Q.4. What are the improvements made in the Mendeleev's periodic table?

Ans IMPROVEMENTS IN MENDELEEV'S PERIODIC TABLE

(i) Atomic Number

The elements were arranged in ascending order of their atomic numbers instead of their atomic masses.

(ii) Extra Group

For the arrangement of Noble gases, one extra group (VIII-A) was added at the extreme right of the periodic table. These gases had not been discovered in Mendeleev's time.

(iii) Sub-group

In Mendeleev's Periodic table, the elements like Be, Mg, Ca, Sr, Ba, and Zn, Cd, Hg were placed in a single vertical group although they possess different properties.

This confusion was removed by dividing the elements in two types of vertical group A and B.

(iv) Position of Isotopes

If the elements are arranged in the order of their increasing atomic masses, it is not possible to accommodate a large number of isotopes. This problem was solved by arranging elements in ascending order of their atomic numbers.

(v) Regular Arrangement of Pairs

Anomalous pairing can be rectified by arranging them in increasing order of their atomic numbers. e.g. $_{18}Ar$ should be placed before $_{19}K$. Similarly $_{27}Co$ should be placed before $_{28}Ni$ and $_{52}Te$ should be placed before $_{53}I$.

The Modern Periodic Table

In modern periodic table, all the elements are arranged in ascending order of their atomic numbers.

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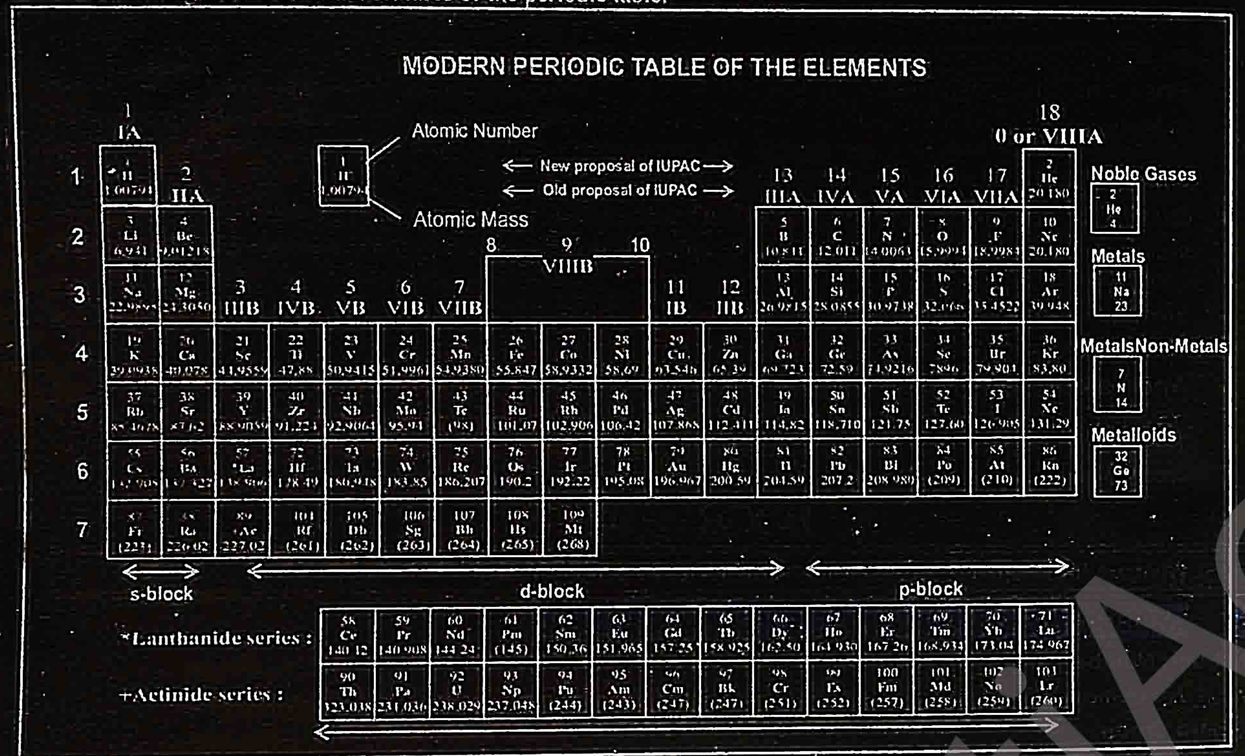
Modern Periodic Law

"If the elements are arranged in ascending order of their atomic numbers, their chemical properties repeat in a periodic manner."

This law was introduced by Moseley in 1911. On the basis of modern periodic law, Bohr introduced modern periodic table.

Essential Features of Modern Periodic Table

Following are the essential features of the periodic table.



1. Groups

Elements with similar properties are placed in vertical columns called groups.

- There are eight (8) groups, which are usually numbered by Roman numerals I to VIII.
- Each group is divided into two sub groups.
  - → **A Subgroups :** Containing representative or normal elements.
  - → **B Subgroups :** Contain less typical elements, called transiton elements and are arranged in the centre of periodic table.
- Elements of same group have similar chemical properties due to same valence shell electronic configuration.
- Usually number of valence electrons is same as that of group number.

2. Periods

"The horizontal rows of elements in periodic table are called periods."

The **essential features** of periods are as follows.

(a) There are 7 periods in the periodic table numbered by Arabic numerals 1 to 7.

(b) The period 1 contains only two elements, hydrogen and helium.

(c) The periods 2 and 3 contain eight elements each and are called short periods. All the elements in these periods are representative elements and belong to A subgroup. In these periods, every eight element resembles in properties with the first element. As lithium and beryllium in the 2nd period resemble in most of their properties with sodium and magnesium of the 3rd period, respectively. Similarly, boron and aluminum both show oxidation state of +3, fluorine in 2nd period has close resemblances with chlorine of 3rd period.

(d) The period 4 and 5 contain eighteen elements each and are called long periods. Out of these, 8 are representative elements which belong to A sub–group. Whereas the other 10 elements, placed in the centre of the table, belong to B subgroup and are known as outer transition elements. In these periods, the repetition of properties among the elements occurs after 18 elements. As after $_{19}K$ (having atomic number 19) the next element with similar properties is $_{37}Rb$.

(e) The period 6 contains thirty-two elements and is called very long period. In this period there are eight representative elements, ten transition elements and a new set of fourteen elements called Lanthanides as they start after $_{57}La$. Lanthanides have remarkably similar properties and are usually shown separately at the bottom of the periodic table.

(f) The period 7 is incomplete so far. It contains only two normal elements $_{87}Fr$ and $_{88}Ra$, ten transition elements and 14 inner transition elements which are called Actinides, as they follow $_{89}Ac$. The actinides are also shown at the bottom of the periodic table under the Lanthanides. Due to their scarcity, the inner transition elements are also called rare earth elements.

Number of elements in different periods

Period	Principal valence shell (n)	Orbitals being filled up	Electrons to be accomodated	Number of elements
First	n = 1	1s	2	2
Second	n = 2	2s, 2p	2+6 =8	8
Third	n = 3	3s,3p	2+6=8	8
Fourth	n = 4	4s,3d,4p	2+10+6	18
Fifth	n = 5	5s,4d, 5p	2+10+6	18
Sixth	n = 6	6s,4f, 5d,6p	2+14+10+6	32
Seventh	n = 7	7s,5f, 6d,7p	2+14 +10+6	32 *

3. Some more Families in the Periodic Table

Families in periods

While studying about periods, it is observed that certain rows of elements with similar properties have assigned common names such as transition elements, Lanthanides, Actinides or Rare Earth elements.

Families in groups

Due to their peculiar characteristics, some typical elements belonging to sub-groups A and B have been assigned family names.

(i) Alkali Metals: Elements of group IA (Li, Na, K, Rb, Cs, Fr) are called alkali metals because of their property to form strong alkalies with water. $2Na + 2H_2O \longrightarrow 2NaOH + H_2$

(ii) Alkaline Earth metals: Elements of group IIA (Be, Mg, Ca, Sr, Ba, Ra) are known as alkaline earth metals because of their presence in Earth's crust and alkaline character.

(iii) Halogens: Elements of group VIIA (F, Cl, Br, I, At) are called halogens due to their salt forming properties.

(iv) Noble gases: The gases of VIIIA group (He, Ne, Ar, Kr, Xe, Rn) are called noble gases because of their least reactivity.

4. Blocks in Periodic Table

Elements in the periodic table can be classified into four blocks. This classification is based upon the valence orbital of the element involved in chemical bonding.

Q.5. How the classification of elements in different blocks helps in understanding their chemistry?

(i) s-block

Elements of IA and IIA subgroups including Helium (He) are called s-block element because their valence electrons are available in "s" orbital. e.g. $_{11}Na = 1s^2, 2s^2, 2p^6, 3s^1$ so, sodium belongs to s-block.

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(ii) p-block

The elements of IIIA to VIIIA except Helium (He) are known as p-block elements as their valence electrons are present in p-orbital $_{17}Cl = 1s^2, 2s^2, 2p^6, 3s^2, 3p^5$ so, chlorine belongs to p-block.

(iii) d-block

In transition elements, electrons in d-orbital are responsible for their valency hence they are called d-block elements $_{26}Fe = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$

(iv) f-block

In Lanthanides and Actinides valence electrons are present in f-orbital hence these elements are called f-block elements $_{58}Ce = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^2$

Importance

This classification is quite useful in understanding the chemistry of elements and predicting their properties especially the concept of valency or oxidation state.

5. Metals, Non-metals and Metalloids

Another basis for classifying the elements in the periodic table is their metallic character.

Metals

- Generally the elements on the left hand side, in the centre and at the bottom of the periodic table are metals.

Non-metals

- Elements in the upper right corner of the periodic table are non-metals.
- In the periodic table elements of groups IVA to VIIIA, at the top right hand corner above the stepped line, are non-metals.

Metalloids

- Some elements; especially lower members of groups, IIIA, IVA and VA have properties of both metals as well as non-metals. These elements are called semi-metals or metalloids.
- The elements just under the "stepped line" such as Si, As, and Te are the metalloids.

Q.14 (a) d and f–Block elements are called transition elements.

Ans The d-block and the f-block elements are called transition elements because they are located between the s and p-block elements and their properties are in transition between the metallic elements of the s-block and nonmetallic elements of the p-block.

Metallic Elements	Nonmetallic elements
Distinguishing luster (shine)	Non-lustrous, various colors
Malleable and ductile (flexible) as solids	Brittle, hard or soft
Conduct heat and electricity	Poor conductors
Metallic oxides are basic, ionic	Nonmetallic oxides are acidic, compounds
Cations in aqueous solution	Anions, oxyanions in aqueous solution

Periodic Trends In Physical Properties

In modern periodic table the elements are arranged in ascending order of their atomic numbers and their classification in groups and periods is based on the similarity in their properties. Yet, due to the gradual increase in the number of protons in the nucleus and electrons in outer shells, the physical and chemical properties of the elements steadily vary within a group or a period. Following are the periodic trends in some physical properties of elements.

The repetition of properties of elements in periodic table after regular intervals is called **periodicity.**

1. Atomic size

(i) Atomic Radius

The half of the distance between the centres of two bonded atoms of any element is called atomic radius.

or

The average distance between the nucleus of an atom and its outermost shell is called atomic radius.

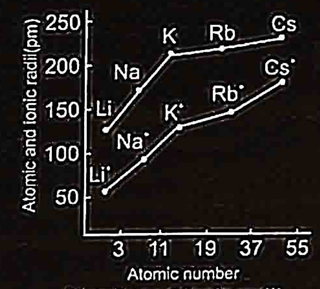
Periodic Trend

(a) Across the Period: Atomic radius decreases left to right in a period. This is because of:

- Increase in atomic number.
- Increase in the positive charge in the nucleus. As positive nuclear charge increases, the negatively charged electrons in the shells are pulled closer to the nucleus.

(b) Down the Group: Atomic radius increases down the group. This is because of:

- Increase in number of shells.
- Increase in shielding effect down the group due to increase in intervening electrons. Thus atomic radius increases.



Atomic and ionic radii of alkali metals

(ii) Ionic Radius

The size of an ion when it is supposed to be spherical is called ionic radius.

Formation of cation

"A cation is formed when an atom lose electron or electrons."

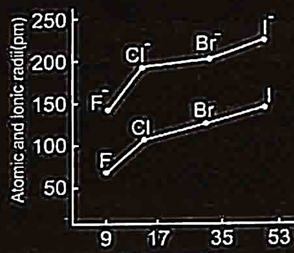
$$A \longrightarrow \underset{\text{cation}}{A^+} + 1e^-$$

Periodic Trend

(a) Across the Period

Within a period isoelectronic positive ions show decrease in ionic radius from left to right because of increasing nuclear charge. $Na^{+1} > Mg^{+2} > Al^{+3}$

similarly $P^{-3} > S^{-2} > Cl^{-1}$



Atomic and ionic radii of halogens.

(b) Down the Group

In the group of the periodic table, similar charged ions increase in size from top to bottom.

Radii of iso-electronic ions

Ion	N^{3-}	O^{2-}	F^-	Na^+	Mg^{2+}
Number of electrons	10	10	10	10	10
Charge on the nucleus	+7	+8	+9	+11	+12
Radius (pm)	171	140	136	95	60

Q.14(b) Lanthanide contraction controls the atomic sizes of elements of 6th and 7th period.

Ans **Lanthanide contraction** is the steady decrease in the size of the atoms and ions of the rare earth elements with increasing atomic number from lanthanum (atomic number 57) through lutetium (atomic number 71). For each consecutive atom the nuclear charge is more positive by one unit, accompanied by a corresponding increase in the number of electrons present in the 4*f* orbitals surrounding the nucleus. The 4*f* electrons very imperfectly shield each other from the increased positive charge of the nucleus, so that the effective nuclear charge attracting each electron steadily increases through the lanthanide elements.

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Q. Why the size of cation is always smaller than its parent atom?

Ans A cation is formed by the loss of one or more electrons from a neutral atom. The size of cation is always smaller than its parent atom. This is because of:

- Removal of one or more electrons from neutral atom usually results in the loss of outermost shell.
- Removal of electrons causes an imbalance in proton electron ratio. Due to greater attraction of nuclear charge, the remaining electrons of ions are drawn closer to the nucleus.

Example $Na \longrightarrow Na^{+} + 1e^{-}$

157 pm 95 pm

Q.7 Why the ionic radii of negative ions are larger than the size of their parent atoms?

Ans When a neutral atom gains one or more electrons, it becomes a negative ion. The size of the ion is increased because of two reasons given below:-

(i) Incoming electron is repelled by the valence electron. So, in order to add this incoming electron, the expansion of the shell takes place which ultimately reduces the repulsion.

(ii) Imbalance in electron and proton ratio occurs.

As a result, the ionic radius of negative ion becomes greater than the size of its parent atom.

Example: $F_{(2,7)} + 1e^{-} \longrightarrow F^{-}_{(2,8)}$

72 pm 136 pm

The radius of F-atom is 72 pm while that of Fluoride ion (F^{-}) is 136 pm.

2. Ionization Energy

"The minimum amount of energy which is required to remove an electron from the outermost shell of an isolated gaseous atom is called ionization energy."

Examples

1. $Na \longrightarrow Na^{+1} + 1e^{-}$ $I = 496\ kJmol^{-1}$
2. Elements with greater number of electrons have more than one values of ionization energy. So for magnesium, the first ionization energy value is the energy required to remove the first electron.

$$Mg \longrightarrow Mg^{+1} + 1e^{-} \quad I_1 = 738\ kJmol^{-1}$$

Similarly, the second ionization energy value is the energy required to remove the second electron:

$$Mg^{+1} \longrightarrow Mg^{+2} + 1e^{-} \quad I_2 = 1451\ kJmol^{-1}$$

Q.8. Why ionization energy decreases down the group and increases along a period?

Factors effecting Ionization Energy

(i) Atomic Size: Atomic size $\propto \frac{1}{I.E}$

(ii) Nuclear charge: Nuclear charge $\propto$ I.E

(iii) Shielding effect: Shielding effect $\propto \frac{1}{I.E}$

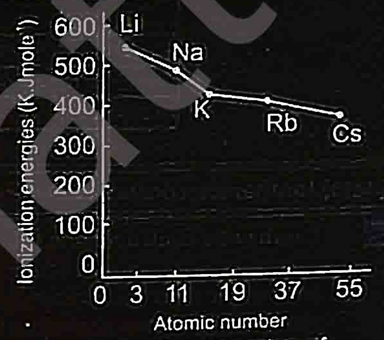
(iv) Stable electronic configuration

(v) Penetration Effect: s > p > d > f

Periodic Trend

(a) Down the group

The value of ionization energy decreases from top to bottom in a group.



Ionization energies of Alkali metals

Due to:

- Addition of an extra shell successively in each period hence more number of electrons shield the nucleus.
- The nuclear charge increases but as the size of the atom and the number of electrons causing the shielding effect also increases therefore ionization energy decreases from top to bottom.

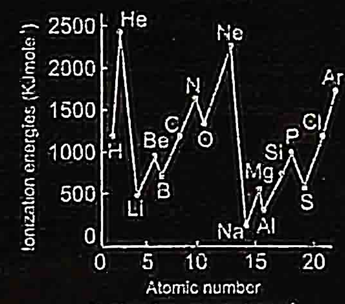
That is why in alkali metals, for example, it is easier to remove an electron from caesium atom than from lithium atom.

Across the period

The value of ionization energy increases from left to right in a period.

Reasons

- Due to decrease in atomic radius nuclear charge increases, more strongly electrons are bound to the nucleus and hence higher the ionization energy of the atom.
- Nuclear charge increases effectively that makes removal of electron difficult and hence value of ionization energy increases.
- Shielding effect almost remains constant.



Ionization energies of elements of short periods.

The figure also reveals that inert gases have the highest values of ionization energy because due to complete outermost shell in them, the removal of electron is extremely difficult.

Q. Why second I.E value is always greater than first I.E value?

Ans: Energy required to remove electron from a unipositive ion is called second ionization energy.

$$Mg \longrightarrow Mg^{+1} + 1e^{-} \quad I_1 = 738\ kJmol^{-1}$$

$$Mg^{+1} \longrightarrow Mg^{+2} + 1e^{-} \quad I_2 = 1451\ kJmol^{-1}$$

The value of second I.E is greater due to

(i) Small cationic radius than parent atom.

(ii) Greater nuclear attraction on the remaining electron.

3. Electron Affinity (E.A)

"The energy released or absorbed, when an electron is added to a valence shell of an isolated gaseous atom to form a negative ion is called electron affinity."

e.g. $F + e^{-} \longrightarrow F^{-}$ E.A. = –337 $kJmol^{-1}$

Factors Effecting the Electron Affinity

Following are the factors which effect the electron affinity.

(i) Atomic size: Atomic size $\propto \frac{1}{E.A}$

(ii) Nuclear charge: Nuclear charge $\propto$ E.A

(iii) Shielding effect: Shielding effect $\propto \frac{1}{E.A}$

(iv) Vacancies in the outermost shell: Relatively smaller atoms with one or two vacancies in the outermost shell show large values of electron affinity.

Periodic Trend

(i) Across the Period

Across the period electron affinity increases due to:

- Increase in atomic number.
- Decrease in atomic radius.
- Shielding effect almost remains same.

(ii) Down the group

When we move from top to bottom in the group, electron affinity decreases due to increase in atomic radius and shielding effect.

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Important Point

Knowledge of electron affinities can be combined with the knowledge of ionization energies to predict which atoms can easily lose electrons and which can accept electrons more readily.

Q.9. Why the second value of electron affinity of an element is usually shown with a positive sign?

Ans Usually the electronegative elements release energy when first electron is added into them. But when a second electron is added in a uni – negative ion, the incoming electron is repelled by the already present negative ion (charge). In order to overcome this repulsion, energy is absorbed during the process. Thus the formation of a di-negative ion is an endothermic process and its electron affinity is shown with positive sign.

$O + e^- \rightarrow O^-$ $\quad E.A_1 = -141\ kJ\ mol^{-1}$

$O^- + e^- \rightarrow O^{-2}$ $\quad E.A_2 = +780\ kJ\ mol^{-1}$

4. Metallic and Non-Metallic character

Elements in periodic table can be divided into metals, non-metals and metalloids.

Characteristics of Metals

- Metals are good conductor of heat and electricity.
- They have tendency to form cation by losing electrons.
- They form basic oxides which give bases when dissolved in water.
  e.g. $Na_2O + H_2O \longrightarrow 2NaOH$ (base)

Q.10. Why metallic character increases from top to bottom in a group of metals?

Periodic Trend of Metallic Character

"The tendency of an element to lose electron and form a positive ion is called metallic character".

- **Down the group:** As it becomes easier to remove the electron of an atom bigger in size, therefore metallic character increases from top to bottom in a given group of elements.
- **Across the period:** Metallic character decreases from left to right across a period. The elements of group VIIA (the halogens) are least metallic in nature.

Characteristics of Non-Metals

- Non-metals are poor conductor of heat and electricity.
- They have tendency to form negative ion (anion) by gaining electron.
- Non-metals form acidic oxides which yield acids when dissolved in water.
- All the gases are nonmetals. e.g. $SO_3 + H_2O \longrightarrow H_2SO_4$

Periodic Trend of Non-Metallic Character

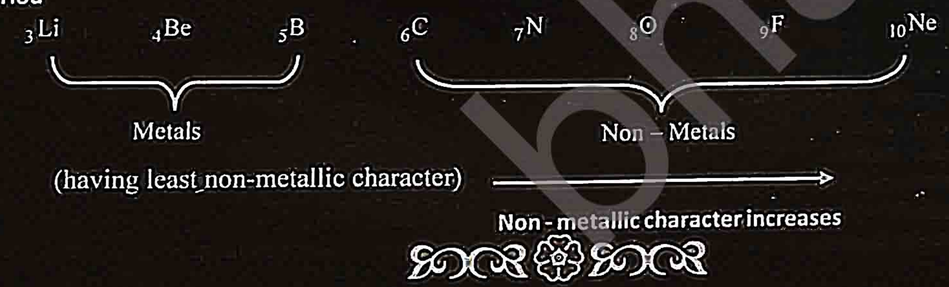
(i) Down the group

- Non-metallic character of an element decreases as the atomic size increases. Therefore in a group of non-metals like halogens, the non-metallic character decreases from top to bottom. The member at the top, fluorine, is the most non-metallic element of the periodic table.
- In the elements of groups VA and VIA, nitrogen and oxygen are pure non-metals and usually exist in gaseous state while bismuth and polonium, the members at the bottom of these groups, are fairly metallic in nature.

(ii) Across the period

Due to decrease in atomic size, gain of electron increases, as a result non-metallic character increases.

2nd Period



Q.11 Explain the variation in melting points along the short periods.

Q.14 c The melting and boiling points of the elements increase from left to the right upto the middle of s-and p-block elements and decrease onward.

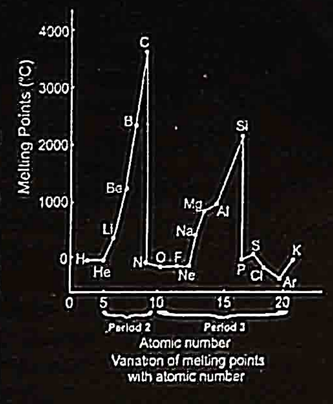
5. Melting and boiling points

Melting and boiling points of elements tell us something about how strong the atoms or molecules in them are bound together.

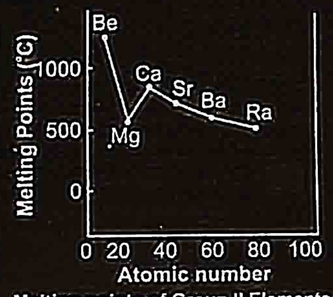
Periodic Trend

(a) Variation in a Period

- **Across the short periods**, melting and boiling points of elements increase with the number of valence electron up to group IVA.
- **The group IA elements** have low melting and boiling point because each atom in them provides only one electron to form a bond with other atom.
- **The group IIA elements** have considerably higher melting and boiling points than those of group IA elements because each atom in them provides two binding electrons.
- **Carbon** has the maximum number of binding electrons, thus it has a very high melting point in diamond in which each carbon is bound to four other carbon atoms. In general, the elements which exist as giant covalent structures have very high melting and boiling points.
- **Melting points of group IVA to VIIA:** When we move from group IVA to group VA, VIA and VIIA as the lighter elements of these groups exist as small, discrete covalent molecules, rather than as three dimensional lattices. For instance, nitrogen, oxygen, and fluorine exist as individual molecules which have very weak intermolecular forces and hence they have extremely low melting and boiling points.



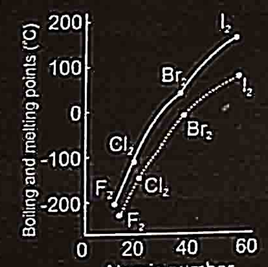
Variation of melting points with atomic number



Melting points of Group II Elements

(b) Variation in a Group

- **The melting and boiling points of IA and IIA group elements** decrease from top to bottom due to increase in their atomic sizes. The binding forces present between large sized atoms are relatively weaker as compared to those between smaller atoms.
- **Group VIIA elements** which exist in the form of molecules, the melting and boiling points increase down the group. This is because large molecule exerts stronger force of attraction due to their higher polarizabilities.



6. Oxidation State

"The Oxidation number of an atom in a compound is the charge (with the sign) which it would carry in the compound."

- **In ionic compounds,** it is equal to the number of electrons gain or lose by the atom. e.g. In sodium chloride oxidation state of Na is +1 and chlorine is –1 i.e. Na^{+1}, Cl^{-1}.
- **In covalent compounds,** it is decided on the basis of difference in their relative electronegativities.
  e.g. $SnCl_4$ is a covalent compound in which oxidation state of Sn is +4 and of Cl is -1.
- **In free state,** (Cl_2, Br_2, O_2, H_2 etc.) oxidation state of elements is zero.

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Periodic Trend

(a) Across the Period

Typical elements (Subgroup A)

The oxidation state of a typical element is directly or indirectly related to the group number to which the element belongs in the periodic table.

(i) The elements of IA to IVA have the same oxidation states as their group numbers are. Just as B, Al and Ga belong to group IIIA, hence, they always show oxidation state of +3. So, for the elements of these groups, the oxidation state is same as the number of electrons present in the valence shells of the elements.

(ii) For the elements of group VA, the oxidation states are either the number of electrons present in the valence shell (which is same as their group number) or the number of vacancies available in these shells. For example, N, P, As and Sb frequently show +3 as well as +5 oxidation states.

(iii) Elements of group VIA show almost similar behaviour. In H_2SO_4 sulphur shows the oxidation state of +6, which is the number of electrons in its outermost shell whereas its oxidation state is -2 in H_2S, which is the number of vacancies in its outermost shell.

(iv) In group VIIA elements, oxidation state is always -1, which is again the number of vacancies in their outermost shells.

(v) Group VIIIA elements, which are also called zero group elements, usually show zero oxidation state because there is no vacancy in their outermost shells.

Transition Elements (Subgroup-B)

Transition elements, which are shown in B subgroups of the periodic table, also show the oxidation states equal to their group number as it can be seen for Cu(I), Zn(II), V(V), Cr(VI) and Mn (VII). But due to greater number of valence electrons available in partly filled d-orbitals, these elements usually show more than one oxidation states in their compounds.

(b) Down the Group

Due to same outermost shell electronic configuration, the elements of same group have same oxidation state.

Q.14 (d) The oxidation states vary in a period but remain almost constant in a group.

Ans Oxidation state of an element depends directly or indirectly on the number of valence electrons or the number of vacancies available in the valence shell.

In a period, when we move from left to right, the number of valence electrons goes on increasing so the oxidation states of elements also change accordingly.

In a group, due to same outermost shell electronic configuration, the elements of same group have same oxidation state.

Q.12. Oxidation state of noble gases is usually zero. Why?

Ans Oxidation state of an element is directly or indirectly related to the number of its valence electrons or the number of vacancies available in its valence shell. In case of noble gases, their outermost shells are completely filled with electrons and no vacancy is available in their outermost shells. Thus, these gases usually show zero oxidation state with reference to which they are often called zero group elements.

7. Electrical Conductance

One of the most familiar properties of metals is their ability to conduct electricity. This property is mainly due to the presence of relatively loose electrons in the outermost shell of element and ease of their movement in solid lattice.

Periodic Trend

(i) The electrical conductance of metals in groups IA and IIA, generally increases from top to bottom. However, the trend is not free from the individual variation in different atoms.

(ii) Metals of group IB, which are known as coinage metals, have extraordinary high values of electrical conductance.

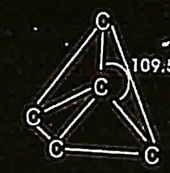
(iii) Nonmetals especially of groups VIA and VIIA, show such low electrical conductance that they can be considered as nonconductors.

(iv) In the series of transition metals, the values of electrical conductance vary so abruptly that no general trend can be assigned to them.

(v) Carbon, in the form of diamond is non-conductor because its valence electrons are tetrahedrally bound and unable to move freely, while in the form of graphite, carbon is fairly good conductor because one of its four valence electrons is relatively free to move.

(vi) The lower elements of group IVA tin and lead, are fairly good conductors and their values of electrical conductivity are comparable with those of their counterparts in group IA.

Q.13. Why diamond is a non-conductor and graphite is fairly a good conductor?

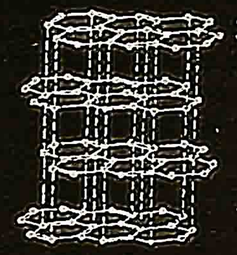


Ans **Diamond as a non-conductor:-**

In diamond, each carbon atom is sp^3 hybridized and forms four sigma bonds with four other carbon atoms. Sigma bond is a very stable bond and σ-electrons are highly localized. They can't move from one place to another. As no free electrons are available in diamond so it is a non-conductor of heat and electricity.

Graphite as a conductor:-

In graphite, each carbon is sp^2 hybridized and forms three σ-bonds with other carbon atoms. Their unhybridized p – orbitals bound to form a π-electrons cloud between two layers of graphite. These π-electrons are highly delocalized so they can conduct electricity parallel to the layers. In graphite hexagonal structure is present. That's why graphite is a good conductor parallel to layers but not perpendicular to the layers.



8. Hydration Energy

"The heat absorbed or evolved when one mole of gaseous ions dissolve in water to give an infinitely dilute solution is called hydration energy."

Example $H^+_{(g)} + H_2O_{(\ell)} \longrightarrow H_3O^+_{(aq)} \quad \Delta H_h = -1075\ kJ\ mol^{-1}$

Factor

Hydration energy highly depends upon charge density (charge to size ratio) of the ions. Greater the charge density higher will be the hydration energy and vice versa.

Periodic Trend

- For a given set of ions, for example of group IA, charge to size ratio decreases from top to bottom in a group, the hydration energy decreases significantly.

$$Li^+ > Na^+ > K^+$$

$$-499\ kJmol^{-1} \quad -390\ kJmol^{-1} \quad -305\ kJmol^{-1}$$

- On the contrary, the hydration energy increases significantly by moving from left to right in a period as the charge to size ratio increases, as found in the metal ions of third period.

$$Na^{+1} < Mg^{+2} < Al^{+3}$$

$$-390\ kJ\ mol^{-1} \quad -1891\ kJmol^{-1} \quad -4613\ kJ\ mol^{-1}$$

Ion	ΔH_h kJ mole^{-1}
Li^+	- 499
Na^+	- 390
K^+	- 305
Mg^{2+}	- 1891
Ca^{2+}	- 1562
Al^{3+}	- 4613
F^-	- 457
Cl^-	- 384
Br^-	- 351
I^-	- 307

Q.14 (e) The hydration energies of the ions are in the following order:

$$Al^{3+} > Mg^{2+} > Na^+$$

Ans Hydration energy depends on charge to size ratio i.e. charge density of the ions. Ions having high charge density have high hydration energies.

On moving from left to right in a period, the charge of iso-electronic +ve ions increases but their size decreases. As Na^+, Mg^{++} and Al^{+3} belong to the same period so same trend is followed in these ions. Al^{+3} being smaller in size have high charge density and consequently possess highest hydration energy. As a result of this the order is:

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Na^{+1} < Mg^{+2} < Al^{+3}

$-390\ kJ\ mol^{-1}$ $-1891\ kJmol^{-1}$ $-4613\ kJ\ mol^{-1}$

Q. Why the hydration energy of Ca^{2+} is less than that of Al^{3+} ion?

PERIODIC RELATIONSHIP IN COMPOUNDS

Halides

Binary compounds of halogens with other elements are called halides.

Classification of Halides

The physical properties of halides are largely determined by the nature of bonding present in them. On the basis of nature of bonding, halides are of following types.

(i) Ionic halides. (ii) Polymeric halides. (iii) Covalent halides.

(i) Ionic halides

Strongly electropositive elements (IA and IIA groups except Be) having greater electronegativity difference with halogen atom, form ionic halides. The halides of group IA are considered purely ionic compounds.

Examples: NaCl, $MgCl_2$, $CaCl_2$, KBr etc.

Properties

- They have high melting and boiling points.
- They have three dimensional lattices consisting of discrete ions.
- They exist in solid state.
- They are conductor of electricity in molten state or aqueous solution.

Variation with halogens

Among the pure ionic compounds, the fluorides have the highest lattice energies due to the small size of fluoride ion. Thus for ionic halides, the fluorides have the highest melting and boiling points which decrease in the order.

Fluoride > Chloride > Bromide > Iodide

(ii) Polymeric halides

In between the ionic or covalent halides, there is another class of halides called polymeric halides. In these halides, the halogen atom acts as a bridge between two atoms of other element.

Less electropositive elements, such as Be, Ga and Al form polymeric halides having partly ionic bonding with layer or chain lattices.

Examples: $BeCl_2$, $AlCl_3$, $GaCl_3$ etc.

Properties

Their properties are intermediate between the covalent and ionic halides.

(iii) Covalent halides

Least electropositive elements of IVA, VA, VIA groups, having less electronegativity difference with halogen atom, form covalent halides.

Examples: CCl_4, NF_3, PCl_3, S_2Cl_2 etc.

AlF_3 $AlCl_3$ $AlBr_3$ AlI_3 →

Covalent character increases as the size of the halide ion increases

Properties

- The intermolecular forces in covalent halide molecules are weak van der Waal's forces.
- They often exist in gases, liquids or low melting point solids.
- They have low melting and boiling points.
- Non-conductor of electricity.
- The lattice of $SiCl_4$ consists of discrete molecules, which are highly polar. The bonds in PCl_3 and S_2Cl_2 are less polar than those of $SiCl_4$.

Variation with halogens

Physical properties of covalent halides are influenced by the size and polarizability of the halogen atom. Iodides, as being the largest and more polarizable ions possess the strongest van der Waal's forces and therefore have higher melting and boiling points than those of others covalent halides.

Periodic Trend

Across the period:

Q.14 (f) Ionic character of halides decreases from left to the right in a period.

Ionic character of halides depends on the electronegativity difference between the halogen and the other atom.

Elements on the left side of the periodic table (Group I-A and II-A elements) are highly electropositive. They have low ionization energy and thus possess the tendency to lose electron easily. They will form ionic bond with the halogens, which are in turn highly electronegative on the right side of periodic table. So, on moving from left to right along the period, elements become less electropositive. Thus, electronegativity difference reduces and the trend is shifted towards covalent halides.

Melting points of chlorides of Period Three Elements and their bonding character

Name of compounds	Property	
	Melting point (°C)	Type of bonding
NaCl	808	Ionic
$MgCl_2$	715	Partly ionic
$AlCl_3$	192	Partly ionic
$SiCl_4$	-68	Partly covalent
PCl_3	-93	Partly covalent
S_2Cl_2	-80	Partly covalent

Down the Group

The variation in boding character is also present in descending from top to bottom in the halogen group. In general, for a metal the order of decreasing ionic character of the halides is:

Fluoride > chloride > bromide >Iodide

For example, AlF_3 is purely ionic compound having melting point 1290°C and fairly a good conductor, whereas, AlI_3 is predominantly covalent with melting point 198°C and electrically a non-conductor.

Variation due to Oxidation States

In case of an element forming more than one halides, the metal halide in its lower oxidation state tends to be ionic, while that in the higher oxidation state is covalent. For example, $PbCl_2$ mainly ionic and $PbCl_4$ is fairly covalent. This can be explained by the higher polarizing power of Pb^{4+} as compare to that of Pb^{2+}

$$\text{Charge density} \propto \frac{\text{charge}}{\text{size}} \propto \text{Polarizinging Power} \propto \text{Polarization}$$

Q. $PbCl_2$ is mainly ionic while $PbCl_4$ is fairly covalent compound. Justify?

Ans **According to Fajan rule:**

Greater the charge density of a cation, greater will be its polarizing power and hence more covalent character it will induce.

$$\text{Charge density} \propto \frac{\text{charge}}{\text{size}} \propto \text{Polarizinging Power} \propto \text{Covalent Character}$$

In $PbCl_4$, due to small size and high charge Pb^{4+} has greater charge density than Pb^{2+} in $PbCl_2$. As a result, Pb^{4+} has more polarizing power and hence $PbCl_4$ is a covalent compound.

Hydrides

The binary compounds of hydrogen with other elements are called hydrides.

Classification of Hydrides

According to the nature of boding, hydrides may be broadly classified into three classes.

(i) Ionic hydrides
(ii) Intermediate hydrides
(iii) Covalent hydrides

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(i) Ionic hydrides

The elements of group IA and the heavier members of group IIA form ionic hydrides. They have ionic bond.

Examples: NaH, CaH_2, KH etc.

Properties

- Ionic hydrides contain H^- (Hydride) ion.
- These hydrides are crystalline solid compounds, with high melting and boiling points.
- These hydrides are conductor of electricity in molten state and aqueous solution.

(ii) Intermediate Hydrides

The elements like Be, Mg, Zn, Cd and In, combine with hydrogen to form intermediate hydrides.

Examples: BeH_2, MgH_2, ZnH_2 etc.

Properties

- Their properties are in between ionic and covalent hydrides.
- They have polymeric structures and covalent in nature.

Hydrides of the elements of IA to VIIA and IIB sub-groups

IA	IIA	IIB	IIIA	IVA	VA	VIA	VIIA
LiH	BeH_2		BH_3	CH_4	NH_3	H_2O	HF
NaH	MgH_2		AlH_3	SiH_4	PH_3	H_2S	HCl
KH	CaH_2	ZnH_2	GaH_3	GeH_4	AsH_3	H_2Se	HBr
RbH	SrH_2	CdH_2	InH_3	SnH_4	SbH_3	H_2Te	HI
CsH	BaH_2			PbH_4	BiH_3		
Ionic		Intermediate		Covalent			

(iii) Covalent Hydrides

The elements having electronegativity values more than 1.8 form covalent hydrides. These hydrides have covalent bond.

Examples: HCl, BH_3, CH_4, H_2O, NH_3 etc.

Properties

- They are usually gases or volatile liquids.
- These hydrides are non-conductor of electricity.
- They are soluble in organic solvents.
- Their bond energies depend on the size and the electronegativity of the elements.
- Stability of covalent hydrides increases from left to right in a period and decreases from top to bottom in a group. e.g. Fluorine forms the most stable hydrides and the least stable hydrides are formed by thallium (Tl), lead (Pb) and bismuth (Bi).
- Since electronegativity of hydrogen is 2.1, most of these hydrides have polar covalent bonds in which hydrogen is carrying a slight positive charge. Due to high polarity, the hydrides like H_2O and HF are capable of forming hydrogen bonds between their molecules.
- The boiling points of covalent hydrides generally increase on descending a group except the hydrides like H_2O, HF and NH_3 which, due to hydrogen bonding have higher boiling points than might be expected.

Melting and boiling points of Hydrides of Groups IVA and VIA

Hydrides	Property	
(Group IVA)	Melting point (°C)	Boiling point (°C)
CH_4	-184	-164
SiH_4	-185	-112
GeH_4	-165	-90
SnH_4	-150	-52

(Group VIA)		
H_2O	0.00	100
H_2S	-82.9	-59.6
H_2Se	-65.7	-41.3
H_2Te	-48	-1.8

Periodic Trend

Across the period

- In ionic hydrides, the tendency towards covalent character increases by moving from left to right in the periodic table.
- Stability of covalent hydrides increase from left to right in a period.
- On moving left to right across a period the electronegativity of the other element increases and the hydrogen element bond becomes more polar.

Down the group

- Stability of the covalent hydrides decrease down the group.
- Boiling points of covalent hydrides increase due to increase in London dispersion forces except H_2O, HF and NH_3 which have high boiling points on the top of their groups.

Q.14 (g) Alkali metals give ionic hydrides.

Ans Alkali metals are more electro-positive than hydrogen. They have a strong tendency to lose electron and form a uni-positive ion. This electron is accepted by hydrogen to form a hydride ion (H^-). These +ve and –ve ions then combine to form an Ionic Bond. That's why alkali metals give ionic hydrides.

Oxides

"The binary compounds of oxygen with other elements in the periodic table are called oxides."

Since, many of these have quite unusual properties, there is an extensive and varied chemistry of the compounds of oxygen.

Classification of Oxides

Oxides can be classified in more than one ways as:

(i) On the basis of nature of bonding.
(ii) On the basis of oxidation state of oxygen.
(iii) On the basis of acidic and basic character.

On the basis of oxidation state of oxygen

Oxides	Oxidation state of oxygen	Example
Normal oxides	-2	Li_2O, MgO, ZnO, Al_2O_3, Cl_2O_7
Peroxides	-1	H_2O_2, Na_2O_2, BaO_2
Super oxides	-1/2	KO_2, RbO_2, CsO_2 etc.
Sub oxides	+2, +4	C_3O_2 (highly unstable)

On the basis of acidic or basic character

On this basis there are following three types of oxides.

(i) Acidic oxides

- Non-metals like C, N, O, P etc. form acidic oxides
- On adding in water, they give acidic solutions.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

Examples: CO_2, P_4O_{10}, SO_3, Cl_2O_7 etc.

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(ii) Basic oxides

- Metals of IA & IIA groups (except Be) form basic oxides.
- On adding in water: they give basic solutions.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

The O^{-2} ion has great affinity for proton (H^+) and cannot exist alone in an aqueous solution. Therefore, it immediately takes proton (H^+) from water and forms OH^- ion. In this way the concentration of OH^- increases and solution becomes basic.

Examples: Li_2O, MgO, CaO etc.

(iii) Amphoteric oxides

The less electropositive elements (Be, Al, Zn, Ga, In) form amphoteric oxides. They behave as bases when react with strong acids and behave as acids with strong bases.

Examples: BeO, Al_2O_3, ZnO, Bi_2O_3 etc.

$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$$

$$ZnO + 2NaOH + H_2O \longrightarrow Na_2[Zn(OH)_4]$$

Classification of oxides based on their acidic and basic character

IA	IIA	IIB	IIIA	IVA	VA	VIA	VIIA
Li	Be		B	C	N	O	F
Na	Mg		Al	Si	P	S	Cl
K	Ca	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Cd	In	Sn	Sb	Te	I
Cs	Ba	Hg	Tl	Pb	Bi	Po	At
Basic Oxides				Amphoteric oxides		Acidic oxides	

Periodic Trend

Across the Period

In a given period, the oxides progress from strongly basic through weakly basic, amphoteric and weakly acidic to strongly acidic.

Example: Na_2O, MgO, Al_2O_3, SiO_2, P_4O_{10}, SO_3, Cl_2O_7

strongly basic · basic · amphoteric · weakely acidic · acidic · acidic · strongly acidic

Down the Group

The basicity of main group metal oxides increases on descending a group of the periodic table.

Example: $BeO < MgO < CaO < SrO < BaO$

- The basicity of transition metal oxides (Sub group B) decreases from top to bottom.

Variation due to Oxidation State

The oxidation state of the metal also affects the acid / base character of its oxides. The acidity increases with increasing oxidation state. e.g. The acidity of $MnO < Mn_2O_3 < MnO_2 < Mn_2O_7$

Q.14 (h) Although both sodium and phosphorous are present in the same period of the periodic table yet their oxides are different in nature, Na_2O is basic while P_2O_5 is acidic in character.

Ans Although Na and P belong to the same period but their metallic character differs a lot. On moving from left to right in a period, the nuclear charge increases due to which the size decreases. This increased nuclear charge is responsible for decreasing the metallic character. As a result Na being a metal forms basic oxide as it yields base in water.

$$Na_2O + H_2O \rightarrow 2NaOH$$

(Base)

While P being a non-metal gives acidic oxide as it yields acid in water.

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$$

Q.6. How do you justify the position of hydrogen at the top of various groups?

The Position of Hydrogen

Position of an element in periodic table depends upon its electronic configuration and properties. Hydrogen resembles the elements of group I-A, IV-A and VII-A in some respects. Properties of hydrogen do not completely match any one of the above-mentioned groups. That is why position of hydrogen is still undecided.

Hydrogen and IA group (Alkali metals)

Similarities

- Hydrogen and alkali metals have one electron in their valence "s" sub-shell, (ns^1).
- Valence shell electronic configuration of hydrogen and alkali metals is same.
- Both hydrogen and alkali metals by losing their valence electron, form uni-positive ion.

$$H \longrightarrow H^+ + 1e^-$$

$$M \longrightarrow M^+ + 1e^-$$

- Both hydrogen and alkali metals have a strong tendency to combine with electronegative elements such as halogens.
- Both form ionic compounds which dissociate in water (ionize in water).
- Both hydrogen and alkali metals are good reducing agents.

Dissimilarities

IA group	Hydrogen
The elements of IA group are metals.	It is a non-metal.
Alkali metals are solid at room temperature.	Hydrogen is a gas at room temperature.
Due to low I.E, they lose electron easily.	Hydrogen does not lose electron as easily as most of the alkali metals.
They do not gain electron.	It gains electron.
They do not exist in the molecular form	Hydrogen exists as H_2 (molecular form) in open atmosphere.
Na^+ and K^+ are stable in water.	H^+ is unstable in water and form H_3O^+ ion.

Hydrogen and VIIA group (Halogens)

Similarities

- Both hydrogen and halogens gain one electron to complete their valence shell. In this way both form uni-negative ions.

$$H + 1e^- \longrightarrow H^- \quad \text{(hydride ion)}$$

$$X + 1e^- \longrightarrow X^- \quad \text{(halide ion)}$$

- Both hydrogen and halogens are non-metals in true sense.
- Both exist as molecular form in open atmosphere (H_2, F_2, Cl_2, Br_2).
- Hydrogen is the gas like that of most halogens (F, Cl).
- Both hydrogen and halogens form stable ionic compounds with alkali metals.

$$H_2 + 2Na \longrightarrow 2NaH$$

$$Cl_2 + 2Na \longrightarrow 2NaCl$$

Dissimilarities

Hydrogen	VIIA group (Halogens)
Hydrogen has one electron in its valence shell.	Halogens have seven electrons in their valence shells.
It loses its valence electron to form hydrogen ion.	They cannot lose electrons.

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$H \longrightarrow H^+ + 1e^-$	
It is a s-block element.	They belong to p-block.
It combines with oxygen to form stable oxides. (H_2O)	They cannot form stable oxides. (ClO_2, Cl_2O_7)
It is a gas at room temperature.	Br_2 is a liquid while Iodine is solid at room temperature.

Hydrogen and IVA group (Carbon family)

Similarities

- Hydrogen has half-filled outermost shell like that of elements of IVA group
- Both hydrogen and elements of IVA group combine with other elements through covalent bonding.
- Like carbon, hydrogen also shows remarkable reducing property.

$$CuO + H_2 \longrightarrow Cu + H_2O$$

$$SnO_2 + C \longrightarrow Sn + CO_2$$

- Ionization energy and electron affinity of hydrogen and carbon are comparable.
- Electronegativity of hydrogen and carbon family are almost similar. [H = 2.1, C = 2.5 , Si= 2.4]

Dissimilarities

Hydrogen	IVA group (carbon family)
Hydrogen belongs to s-block.	The elements of IVA group belong to p-block.
It is a gas at room temperature.	IVA group elements are solid at room temperature.
It needs one electron to complete its valence shell.	Elements of IVA group need 4 electrons to complete their valence shell.
It does not form long chain compounds.	Carbon and Si form long chain compounds when they combine with their atoms. (catenation).
Due to one electron in the valence shell, hydrogen can combine with only one element at a time.	Carbon can simultaneously form bonds with more than one elements.

Conclusion

Some of the properties of hydrogen are similar to those of the elements of IA, IVA and VIIA groups. But this is a fact that hydrogen is a unique element whose properties do not match exactly with any of the groups in the periodic table. However due to partial resemblance in properties with alkali metals and monovalent nature, hydrogen is usually placed at the top of the elements in group IA.

KEY POINTS

1. Although a number of chemists attempted to classify the elements but Dmitri Mendeleev gave the most useful and comprehensive classification.
2. In Mendeleev's Periodic Table, the elements were arranged in ascending order of their atomic weights.
3. The modern periodic law states "if the elements are arranged in ascending order of their atomic numbers, their chemical properties repeat in periodic manner."
4. In modern periodic table, elements with similar properties are placed in eight vertical columns called group. Each group is divided into two sub-groups A and B. Normal or typical elements are placed in sub-group-A and transition elements are placed in sub-group-B.
5. The seven horizontal rows of the periodic table are called "periods".
6. Metals of sub-group I-A and II-A are called alkali metals and alkaline earth metals, respectively. Members of sub-group VII-A are called "Halogens".
7. Due to their less reactivity the elements shown in sub-group VIII-A are called "Noble Gases".
8. Elements of periodic table can also be classified into s-block, p-block, d-block and f-block elements depending upon their valence orbital which is in the process of completion.
9. Elements of periodic table can also be divided into metals, non-metals and metalloids depending upon their properties.
10. Hydrogen is unique element of the periodic table. Due to similarities in properties, it can be placed at the top of group I-A or IV-A or VII-A.
11. Atomic radii increases form top to bottom in a group and decreases along a period.
12. Positive ions are always smaller than their parent atoms while the negative ions are usually larger than the atoms from which they form.
13. Ionization energies increase along a period and decrease down the group.
14. Electron affinities generally increase with increasing atomic number within a period and decrease from lighter to heavier elements in a given group.
15. Metallic character of elements increases down the group and decreases along a period.
16. The oxidation state of a typical element is directly or indirectly related to the group number to which the element belongs in the periodic table.
17. The electrical conductance of an element depends upon the number of free or moveable electrons.
18. There are three types of halides: ionic, polymeric and covalent. Halides of group I-A are ionic in nature, have three dimensional lattices with high melting and boiling points.
19. There are three types of hydrides formed by the elements of Periodic Table: ionic, intermediate and covalent.
20. Highly polar hydrides show hydrogen bonding in them.
21. Oxides may be divided on the basis of their acidic, basic or amphoteric character.
22. Metallic oxides are basic in character, non-metallic oxides are acidic in character and oxides of less electropositive elements like Zn and Pb are amphoteric.

SOLVED OBJECTIVE EXERCISE

Q1. Fill in the blanks.

(i) Mendeleev in his periodic table, arranged the elements according to their atomic _____.
(ii) Vertical columns in modern periodic table are called _____ and horizontal rows are called _____.
(iii) Members of group VIIA are called _____ and alkali metals is the family name of _____ group members.
(iv) Metals form _____ oxides and non-metals form _____ oxides.
(v) Hydrogen can be placed above the groups _____ of the periodic table.
(vi) Shielding effect is actually the _____ due to electrons in between the nucleus and the outermost shell
(vii) Noble gases have the _____ values of ionization energy due to their complete outermost shells.
(viii) When a second electron is added to a uninegative ion, the incoming electron is _____ by the already present negative charge.
(ix) Due to having partly filled d-orbitals _____ metals usually show variable valency.
(x) Melting and boiling points of halogens _____ down the group.

Answer Key.

(i)	Masses	(ii)	Groups, periods
(iii)	Halogens , IA	(iv)	Basic, acidic
(v)	IA, VII A, IV A.	(vi)	Repulsion
(vii)	Highest	(viii)	Repelled
(ix)	Transition	(x)	Increase

Q2. Indicate True or False.

(i) In Mendeleev's periodic table elements Be, Mg, Zn and Cd are placed in the same group.
(ii) The second and third periods contain eighteen elements each.

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(iii) Alkaline earth metals are present in Group IIA.
(iv) Metals are present in the top right corner of the periodic table.
(v) Metalloids are present in the lower half of Group IVA, VA and VIA.
(vi) Hydrogen forms uninegative ion like halogens.
(vii) Oxidation state of an elements is related to the number of period it belongs.
(viii) Diamond is a good conductor of electricity.
(ix) Melting points of halogens decrease down the group.
(x) Zinc oxide is an example of amphoteric oxide.

Answer Key.

(i)	True	(ii)	False	(iii)	True	(iv)	False	(v)	True
(vi)	True	(vii)	False	(viii)	False	(ix)	False	(x)	True

Q3. Multiple Choice Questions. Encircle the correct answer.

(i) Keeping in view the size of atoms, which order is the correct one.
a) Mg > Sr b) Ba > Mg c) Lu > Ce d) Cl > I

(ii) Mark the correct statement.
a) Na^+ is smaller than Na atom b) Na^+ is larger than Na atom
c) Cl^- is smaller than Cl atom d) Cl^- (ion) and Cl (atom) are equal is size

(iii) Mark the correct statement.
a) All lanthanides are present in the same group.
b) All halogens are present in the same period.
c) All the alkali metals are present in the same group.
d) All the noble gases are present in the same period.

(iv) Which statements is incorrect.
a) All the metals are good conductor of electricity. b) All the metals are good conductor of heat.
c) All the metals form positive ions. d) All the metals form acidic oxides.

(v) Which statement is correct.
a) Hydrogen resembles in properties with IA, IVA, and VIIA elements.
b) Hydrogen resembles in properties with IIIA, IVA, and VA elements.
c) Hydrogen resembles in properties with IIA, IVA, and VIA elements.
d) Hydrogen resembles in properties with IIA, IIIA, and VIIA elements.

(vi) Mark the correct statements.
a) The ionization energy of calcium is lower than that of barium.
b) The ionization energy of calcium is lower that that of magnesium.
c) The ionization energy of calcium is higher than that of beryllium.
d) The ionization energy of calcium is lower than that of strontium

(vii) Mark the correct statement.
a) Electron affinity is a measure of energy required to remove the electron.
b) Electron affinity is a measure of energy released by adding an electron.
c) Electron affinity is a measure of energy required to excite an electron.
d) Electron affinity is a measure of energy released by removing an electron.

(viii) Mark the correct statement.
a) Metallic character increases down the group.
b) Metallic character increases from left to right along a period.
c) Metallic character remains the same from left to right along a period.
d) Metallic character remains the same down the group.

(ix) Mark the correct statement.
a) Melting points of halogens decrease down the group.
b) Melting points of halogens increase down the group.
c) Melting points of halogens remain the same throughout the group.
d) Melting points of halogens first increase and then decrease down the group.

(x) Mark the correct statement.
a) Covalent character of metal halides increases from left to right in a period.
b) Boiling points of Group IVA hydrides decrease down the group.
c) Ionic character of hydrides increases from left to right in a period.
d) The basicity of group IIA oxides decreases on descending the group.

Solved Exercise MCQ's

Q. No	Answer	Reason
(i)	(b) Ba > Mg	Size of atoms increase down the group and decrease across a period.
(ii)	(a) Na^+ is smaller than Na atom	Size of cation is smaller than its parent atom.
(iii)	(c) All the alkali metals are present in the same group	Alkali metals are IA group elements which are Li, Na, K, Rb, Cs, Fr.
(iv)	(d) All the metals form acidic oxides	Metal oxides are not acidic but are basic in nature.
(v)	(a) Hydrogen resembles in properties with IA, IVA and VIIA elements	The resemblance of hydrogen with these elements is because of different properties.
(vi)	(b) The I.E of calcium is lower than that of magnesium.	Ionization energy value decreases down the group due to increase in size.
(vii)	(b) Electron affinity is a measure of energy released by adding an electron.	Electron affinity is energy absorbed or released when addition of electron takes place.
(viii)	(a) Metallic character increases down the group.	Due to increase in atomic size, metals lose electrons easily.
(ix)	(b) Melting point of halogens increase down the group.	As the size of halogens increase, intermolecular forces become stronger so melting point increases
(x)	(a) Covalent character of metal halides increases from left to right in a period.	Across a period, electropositive character of metals decreases so covalent character increases.

Previous Board Questions

1. ZnO is amphoteric oxide. Prove by means of reactions.
2. Why Ionization Energy decreases down the group and increases along a period?
3. Hydration energy increases from left to right in a period. Why?
4. $PbCl_2$ is mainly ionic and $PbCl_4$ is fairly covalent. Why?
5. Why the second value of electron affinity of an element is usually shown with a positive sign?
6. What is Mendeleev's periodic table?
7. Why cation is smaller than its parent atom?
8. Why metallic character increases from top to bottom in a group of metals?
9. The hydration energy of Al^{+3} is three times greater than that of Ca^{+2} why?
10. Give the reason. Why the radius of fluorine atom is smaller than that of fluoride ion
11. Why the oxidation sate of noble gases is usually zero?
12. Why hydrogen can be placed at the top of group I-A elements in the periodic table?

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13. Define Dobereiner's law of triads. Also give two examples.
14. Name different classes of oxides and mention trend of oxides across the period?
15. The basic character of oxides decreases from left to right in a period, why?
16. State the modern periodic law.
17. The melting and boiling points of the elements increase from left to the right up to the middle of s-block elements and decrease onwards. Why?
18. The hydration energies of the ions are in the following order.
$Al^{3+} > Mg^{2+} > Na^{+}$
19. Zn, Cd, Hg were placed with Alkaline earth metals in Mendeleev's table. How this confusion is removed in modern periodic table?
20. What are the improvements made in the Mendeleev's periodic table?
21. What is Lanthanide contraction?

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CHAPTER 2

s – BLOCK ELEMENTS

s-block Elements

Metals of group IA and IIA including hydrogen and helium are called s-block elements. They are called the s-block elements because s-orbitals are being filled in their outermost shells.

Q. Why we use the term alkali metals and alkaline earth metals?

Alkali Metals

The name "alkali" came from Arabic, which means "The ashes". The Arabs used this term for these metals because they found that the ashes of plants were composed chiefly of sodium and potassium.

Alkali metals include the elements lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs) and francium (Fr). These are very reactive metals, produce strong alkaline solutions with water.

Alkaline earth metals

The elements of IIA group are called alkaline earth metals. They include beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra). They are called alkaline earth because they produce alkalies in water and are widely distributed in earth's crust in the form of carbonates and silicates.

Q. Write down electronic configuration and physical constants of alkali metals and alkaline earth metals.

Alkali metals

- Alkali metals have only one electron in 's' orbital of their valence shell. (ns^1)
- Because of low ionization energy values, all alkali metals lose their one electron of the valence shell to form monopositive ions 'M$^+$'. $Na \longrightarrow Na^+ + e^-$
- They form ionic compounds and show +1 oxidation state.

$$Na + \frac{1}{2}Cl_2 \longrightarrow NaCl$$

Electronic Configuration of alkali metals

Element	Symbol	At. Number	Electronic Configuration
Lithium	Li	3	$1s^2, 2s^1$
Sodium	Na	11	$1s^2, 2s^2, 2p^6, 3s^1$
Potassium	K	19	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$
Rubidium	Rb	37	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^1$
Cesium	Cs	55	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^1$
Francium	Fr	87	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^1$

Physical constants of group IA (alkali metals)

Properties	Li	Na	K	Rb	Cs
Atomic Number	3	11	19	37	55
Melting points °C	187	97.5	63.6	39.0	28.5
Boiling points (°C)	1325	889	774	688	690
Atomic radius (pm)	123	158	203	216	235
Ionic radius of + 1 ion (pm)	60	95	133	148	169

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Ionization Energy (kJ/mole)	520	496	419	403	376
Density gm/ cm^3 at (20°C)	0.53	0.97	0.86	1.53	1.9
Heat of Hydgation (kJ/mole)	505	475	384	345	310
Electron affinity (kJ/mole)	60	53	48	47	46
Electronegativity	1.0	0.9	0.8	0.8	0.7

In going down the group, the number of shell increases by one at each step and equal to the number of the period to which the element belongs.

Alkaline earth metals

- Alkaline earth metals have two electrons in 's' orbital of their valence shell.
- All alkaline earth metals lose their two electrons to form di-positive ions M^{++}, because their ionization energy values are low.
- They form ionic compounds and show +2 oxidation state.

$$M \longrightarrow M^{2+} + 2e^-$$
$$Ca \longrightarrow Ca^{2+} + 2e^-$$
$$Mg \longrightarrow Mg^{2+} + 2e^-$$
$$Ca + Cl_2 \longrightarrow CaCl_2$$

Electron Configuration of Alkaline Earth Metals

Element	Symbol	At.Number	Electronic Configuration
Beryllium	Be	4	$1s^2, 2s^2$
Magnesium	Mg	12	$1s^2, 2s^2, 2p^6, 3s^2$
Calcium	Ca	20	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$
Strontium	Sr	38	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2$
Barium	Ba	56	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2$
Radium	Ra	88	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2$

Physical constants of group IIA (alkaline earth metals)

Properties	Be	Mg	Ca	Sr	Ba
Atomic Number	4	12	20	38	56
Melting points °C	1289	649	839	769	725
Boiling points (°C)	2970	1107	1484	1384	1640
Atomic radius (pm)	89	136	174	191	198
Ionic radius of + 2 ion (pm)	31	65	99	113	135
Density gm/ cm^3 at (20°C)	1.85	1.74	1.55	2.6	3.5
Heat of Hydration (kJ/mole)	2337	1897	1619	1455	1250
Electron affinity (kJ/mole)	240	230	156	168	52
Ionization energy (kJ/mole)	899	738	590	549	503
Electronegativity	1.5	1.2	1.0	1.0	0.9

Q. Write down the occurrence of alkali metals and alkaline earth metals.

Occurrence of alkali metals (Group IA)

Due to high reactivity, the alkali metals occur in nature in the combined state. None of the alkali metals is found free in nature.

- **Sodium and potassium** are abundant alkali metals and each constitutes about 2.4 percent of the earth's crust. Most of the earth's crust is composed of insoluble alumino-silicates of alkali metals.
- **Lithium** deposits, usually in the form of complex minerals, are widely scattered over the earth. An important commercial source of lithium is the mineral spodumene $LiAl(SiO_3)_2$.
- Small amounts of **rubidium and caesium** are found in potassium salts deposits.
- **Francium** has not been found in nature. It has been prepared artificially in the laboratory and is very unstable, so that a very little is known about this metal.

Occurrence of alkaline earth metals (Group IIA)

Being very reactive, alkaline earth metals also do not occur in free state. The compounds of these metals occur widely in nature.

Common Minerals of the Most Important Alkali Metals

Name of Mineral	Chemical Formula
Lithium	
Spodumene	$LiAl(SiO_3)_2$
Sodium	
Rock Salt (Halite)	NaCl
Chile saltpetre	$NaNO_3$
Natron	$Na_2CO_3.H_2O$
Trona	$Na_2CO_3.2NaHCO_3.2H_2O$
Borax	$Na_2B_4O_7.10H_2O$
Potassium	
Carnallite.	$KCl.MgCl_2.6H_2O$
Sylvite	KCl
Alunite (Alum Stone)	$K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$

- **Magnesium and calcium** are very abundant in earth's crust. The outer portion of the earth was originally in the form of silicates and alumino-silicates of alkaline earth metals. Magnesium and calcium, with sodium and potassium are present in the rocks as cations.
- Magnesium halides are found in sea water.
- Magnesium is an essential constituent of chlorophyll.
- Calcium phosphate $Ca_3(PO_4)_2$ and calcium fluoride CaF_2 are also found as minerals.
- Calcium is an essential constituent of many living organisms. It occurs as skeletal material in bones, teeth, sea-shells and egg shells.
- **Radium** is a rare element. It is of great interest because of its radioactive nature.

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Common Minerals of the Alkaline Earth Metals

Name of Mineral	Chemical Formula
Beryllium	
Beryl	$Be_3Al_2(SiO_3)_6$
Chrysoberyl	Al_2BeO_4
Magnesium	
Magnesite	$MgCO_3$
Dolomite	$MgCO_3.CaCO_3$
Carnallite	$KCl.MgCl_2.6H_2O$
Epsom Salt (Epsomite)	$MgSO_4.7H_2O$
Soap Stone (talc)	$H_2Mg_3(SiO_3)_4$
Asbestos	$CaMg_3(SiO_3)_4$
Calcium	
Calcite (Lime Stone)	$CaCO_3$
Gypsum	$CaSO_4.2H_2O$
Fluorite	CaF_2
Phosphorite	$Ca_3(PO_4)_2$
Strontium	
Strontionite	$SrCO_3$
Barium	
Barite	$BaSO_4$

Q.4 (b) Discuss the peculiar behaviour of lithium with respect to the other members of alkali metals.

Peculiar behaviour of Lithium

Causes of Peculiar behaviour

In many properties lithium has different behaviour from other members of group IA. The deviation from the regular trend is due to the following reasons.

(i) Atomic radius of lithium (123pm) is very small as compared to the other members of group I.

(ii) Li^+ ion has greater charge density.

(iii) The nuclear charge of Li^+ ion is screened only by a shell of two electrons.

The so-called 'anomalous' properties of lithium are due to the fact that lithium is unexpectedly far less electropositive than sodium.

Differences of Lithium from other Alkali Metals

1. Lithium is much harder and lighter than the other alkali metals.
2. The lithium salts of anions with high density are generally less soluble in water than those of the other alkali metals, e.g., LiOH, LiF, Li_3PO_4, Li_2CO_3.
3. Lithium forms stable complex compounds, although complex formation generally is not a property of alkali metals. One of the stable complexes formed by lithium is $[Li(NH_3)_4]^{+1}$
4. Lithium reacts very slowly with water, while other alkali metals react violently.

$$2Li + 2H_2O \longrightarrow 2LiOH + H_2$$

5. Lithium salts of large polarizable anions are less stable than those of other alkali metals. Unlike other alkali metals lithium does not form bicarbonate, tri-iodide or hydrogen sulphide at room temperature.
6. When burnt in air lithium forms only normal oxide, whereas the others form peroxides or super oxides.

$$4Li + O_2 \longrightarrow 2Li_2O \text{ (Lithium oxide)}$$

$$2Na + O_2 \longrightarrow Na_2O_2 \text{ (Sodium peroxide)}$$

7. Lithium hydride (LiH) is more stable than the hydrides of other alkali metals.
8. Lithium compounds are more covalent, that is why its halides are more soluble in organic solvents and the alkyls and aryls of lithium are more stable than those of other alkali metals.
9. Lithium is the least reactive metal of all the alkali metals.
10. When acetylene is passed over strongly heated lithium, it does not produce lithium acetylide, but other alkali metals form the corresponding metallic acetylides.

$$2Na + C_2H_2 \longrightarrow \underset{\text{Sodium Acetylide}}{Na^+C^- \equiv C^-Na^+} + H_2$$

11. Lithium has low electropositive character, thus its carbonate and nitrate are not so stable and therefore decompose giving lithium oxide. Carbonates of other alkali metals do not decompose. Decomposition of lithium nitrate gives different products than the nitrates of other alkali metals.

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$

$$4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$$

$$2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$$

12. Lithium hydroxide when strongly heated, forms lithium oxide but the other alkali metal hydroxides do not show this behaviour.

$$2LiOH \xrightarrow{\text{Red hot}} Li_2O + H_2O$$

13. Lithium reacts with nitrogen to form nitride while the other members of the group do not give this reaction.

$$6Li + N_2 \longrightarrow 2Li_3N$$

14. Lithium chloride (LiCl) has an exothermic heat of solution, whereas chlorides of sodium and potassium have endothermic heats of solution.
15. Lithium carbide (Li_4C) is the only alkali metal carbide formed readily by direct reaction.

$$4Li + C \longrightarrow Li_4C$$

Substance	Heat of solution
LiCl	- 35.0 kJ/mol
NaCl	+ 4.98 kJ/mol
KCl	+ 17.8 kJ/mol
KI	+ 21.4 kJ/mol

MCQ's
Which has least solubility:
(a) CsF (b) LiF
(c) NaF (d) KF
[LiF has nigh lattice energy]

Q6. Compare the chemical behaviour of lithium with magnesium.

Ans **DIAGONAL RELATIONSHIP OF LITHIUM WITH MAGNESIUM:**

The elements of second period resemble in many respect to those of elements of third period which are diagonally opposite to them. This resemblance is called **diagonal relationship.**

	IA	IIA	IIIA	IVA
2nd period	Li	Be	B	C
3rd period	Na	Mg	Al	Si

Comparison of Lithium and Magnesium

Li	Mg
Ionic radius of Li is 0.60 A°	Ionic Radius of Mg is 0.65A°
Carbonate of Li is insoluble in water and decomposes on heating $Li_2CO_3 \rightarrow Li_2O + CO_2$	Magnesium carbonate is insoluble in water and decomposes on heating $MgCO_3 \rightarrow MgO + CO_2$
Lithium reacts with water to form hydroxide and hydrogen $2Li + 2H_2O \rightarrow 2LiOH + H_2$	Magnisum reacts with water to form hydroxide and hydrogen $Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$
Lithium reacts with acids to evolve hydrogen $2Li + 2HCl \rightarrow 2LiCl + H_2$	Magnesium reacts with acids to release hydrogen $Mg + 2HCl \rightarrow MgCl_2 + H_2$
Hydroxides and Nitrates of Lithium decompose on heating	Hydroxide and Nitrate of Mg decompose on heating $Mg(OH)_2 \xrightarrow{\Delta} MgO + H_2O$

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$LiOH \xrightarrow{\Delta} Li_2O + H_2O$ $4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$	$2Mg(NO_3)_2 \xrightarrow{\Delta} 2MgO + 4NO_2 + O_2$
Atomic radius of Li is 123pm	Atomic radius of Mg is 136pm

Q7. (a) Mention the properties of beryllium in which it does not resemble with its own family.

Peculiar behaviour of Beryllium

Beryllium is the lightest member of the series and differs from the other group IIA elements in many ways. This is due to its small atomic size and comparatively high electronegativity value.

The main points of difference are:

1. Beryllium metal is almost as hard as iron and hard enough to scratch glass. The other alkaline earth metals are much softer than beryllium but still harder than the alkali metals
2. The melting and boiling points of beryllium are higher than other alkaline earth metals.
3. As reducing agents, the group IIA metals are all powerful enough to reduce water, at least in principle. However, with water, beryllium forms insoluble oxide (BeO) coating that protects it from further attack.
4. Beryllium in particular is quite resistant towards complete oxidation, even by acids, because of its BeO coating.
5. Beryllium is the only member of its group which reacts with alkalies to give hydrogen. The other members do not react with alkalies.

$$Be + 2NaOH \longrightarrow \underset{\text{Sodium beryllate}}{Na_2BeO_2} + H_2$$

6. Be forms amphoteric oxide while other members form basic oxides.

Trends in Chemical Properties of Alkali Metals

1. Ionization energy

Low ionization energies make the alkali metals, the most reactive family of metals. They are highly electropositive.

2. Oxidation state

Very high second ionization energies indicate that oxidation number higher than +1, are ruled out for the alkali metals.

3. Solubility

The cations of alkali metals e.g., Na^+, K^+, Rb^+ have low charge and large radii than the radius of any cation from the same period, so the lattice energies of their salts are relatively low. Consequently, most of the simple salts of the alkali metals are water-soluble. Most of the salts are dissociated completely in aqueous solution and the hydroxides are among the strongest bases available.

4. Reactions with oxygen

They react with oxygen and the surface is tarnished due to the oxides formed.

- **Lithium** burns in air to form the normal oxide, Li_2O (white solid).

$$4Li + O_2 \longrightarrow 2Li_2O \quad \text{(Lithium oxide)}$$

The exposed metals are oxidized almost immediately by oxygen in air and in the presence of moisture, the oxides formed react with CO_2 in the atmosphere to form carbonates.

$$\underset{\text{Lithium oxide}}{Li_2O} + CO_2 \longrightarrow \underset{\text{Lithium carbonate}}{Li_2CO_3}$$

- **Sodium** will undergo a similar reaction, but only if the supply of oxygen is limited.

$$4Na + O_2 \xrightarrow[\text{oxygen}]{\text{Limited supply of}} 2Na_2O$$

- Reducing property of an element depends upon the ionization energy value. Elements with low ionization energy value are good reducing agents. e.g. Alkali metals

MCQ's

Strongest reducing agent amongst alkali metals in solutions is:
(a) Li (b) Na
(c) K (d) Cs

MCQ's

Na_2O_2 has light yellow colour. This is due to:
(a) presence of unpaired electron in the molecule
(b) presence of trace of NaO_2
(c) presence of KO_2 as an impurity
(d) none of the above

In the presence of excess of oxygen, sodium forms the pale yellow peroxide.

$$2Na + O_2 \xrightarrow[\text{oxygen}]{\text{Abundant supply of}} \underset{\text{Sodium peroxide (Pale Yellow)}}{Na_2O_2}$$

- **Potassium, rubidium and caesium** react with oxygen to form super oxides.

$$K + O_2 \longrightarrow \underset{\text{Potassium super oxide (Orange yellow)}}{KO_2}$$

Caesium explodes spontaneously when it is in contact with air or oxygen.

5. Reactions with water

Very rapid and exothermic reactions occur when alkali metals react with water. A small piece of sodium (potassium or lithium) floated on water reacts vigorously to liberate hydrogen and produce metal hydroxide. The energy produced by the reaction may even ignite the hydrogen.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

The reaction becomes increasingly vigorous from lithium to caesium. Potassium, rubidium and caesium are so highly reactive that they react with ice even at –100°C.

6. Reactions with hydrogen

Alkali metals form ionic hydrides with hydrogen. In ionic hydrides, oxidation state of hydrogen is –1.

$$2M + H_2 \longrightarrow 2M^+H^-$$

- **Rubidium and caesium** react violently with hydrogen at room temperature. The other three metals require high temperature in order to form the hydride.
- **Lithium and sodium** hydrides are useful sources of hydrogen when treated with water.

$$LiH + H_2O \longrightarrow LiOH + H_2$$

Due to the presence of hydride ion (H^-), the ionic hydrides are used as powerful reducing agents.

7. Reaction with nitrogen and carbon

Lithium is the only group IA metal that combines with nitrogen and carbon to form nitride and carbide respectively.

$$6Li + N_2 \longrightarrow 2Li_3N \text{ (Lithium nitride)}$$
$$4Li + C \longrightarrow Li_4C \text{ (Lithium carbide)}$$

Flame Colouration

Element	Flame Colour
Li	Crimson red
Na	Golden yellow
K	Pale violet
Rb	Red violet
Cs	Violet

8. Reactions with halogens

Alkali metals react easily with halogens to give halides.

- **Lithium and sodium** react slowly with chlorine at room temperature. **Molten sodium burns with brilliant yellow flame in a chlorine atmosphere to form sodium chloride.**

$$2Na + Cl_2 \longrightarrow 2NaCl$$

- **Potassium, rubidium and caesium** react vigorously with all the halogens, forming metal halides.

9. Reactions with sulphur

All alkali metals form their sulphides when treated with molten sulphur.

$$2M + S \longrightarrow M_2S$$
$$2Na + S \longrightarrow Na_2S$$

Q.9. (b) What happens when:
i. Lithium carbonate is heated.
ii. Lithium hydroxide is heated to red hot.
iii. Beryllium is treated with sodium hydroxide.
iv. Lithium hydride is treated with water.

Ans (i) $Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$
(ii) $2LiOH \xrightarrow{\text{Red Hot}} Li_2O + H_2O$
(iii) $Be + 2NaOH \longrightarrow Na_2BeO_2 + H_2$
(iv) $LiH + H_2O \longrightarrow LiOH + H_2$

Q. Why sodium is stored in kerosene oil?

Ans Sodium is an alkali metal. Due to low ionization energy it is highly reactive metal. When exposed to air, it immediately forms Na_2O_2. Similarly with water, it forms NaOH and hydrogen gas. Kerosene oil is a mixture of

alkanes which are least reactive compounds. So, sodium in kerosene oil remains inert and kerosene oil can be a useful medium for its storage.

Trends in Chemical Properties of Alkaline Earth Metals

1. Reactions with air

The alkaline earth metals burn in oxygen to form normal oxides except barium which forms peroxide.

- **Beryllium** is the least reactive metal in the group. It is resistant to complete oxidation and stable in air at ordinary temperature but oxidizes rapidly at about 800°C. Therefore beryllium is not tarnished by atmospheric attack but the metal soon loses the silvery appearance.

$$2Be + O_2 \xrightarrow{800°C} 2BeO$$

- **Magnesium** when exposed to air, quickly becomes coated with the layer of MgO. This layer protects the surface from further corrosion at ordinary temperature.

$$2Mg + O_2 \longrightarrow 2MgO$$

When magnesium is burnt in air, a small amount of nitride (Mg_3N_2) is also formed along with magnesium oxide.

- When **barium** is heated in air or oxygen at 500 - 600°C, its peroxide is formed.

$$Ba + O_2 \xrightarrow{500-600°C} \underset{\text{Barium peroxide}}{BaO_2}$$

2. Reactions with hydrogen

Hydrides are produced by treating the molten alkaline earth metals with hydrogen, usually under high pressure.

- Magnesium reacts with hydrogen at high pressure and in the presence of a catalyst (MgI_2) forming magnesium hydride.

$$Mg + H_2 \xrightarrow[(MgI_2)]{\text{Pressure}} MgH_2$$

Similarly $Ca + H_2 \longrightarrow CaH_2$

3. Reactions with nitrogen

All Group II-A elements react with nitrogen on heating giving nitrides. For example, magnesium reacts with nitrogen to give magnesium nitride.

$$3Mg + N_2 \longrightarrow Mg_3N_2 \text{ (Magnesium nitride)}$$

The nitrides hydrolyse vigorously when treated with water, giving ammonia and the respective hydroxides.

$$Mg_3N_2 + 6H_2O \longrightarrow 2NH_3 + 3Mg(OH)_2$$

4. Reactions with sulphur

Elements of group II-A react with sulphur to form metal sulphides, e.g.

$$Mg + S \longrightarrow MgS \text{ (magnesium sulphide)}$$

5. Reactions with halogens

All group II-A elements react directly with halogens giving halides of the type MX_2, e.g.

$$Ca + Cl_2 \longrightarrow CaCl_2$$

6. Reactions with water

- **Beryllium** does not react with water even at red hot temperature.
- **Magnesium** is more reactive than beryllium, even though it is no attacked by cold water. Magnesium reacts slowly with boiling water and quite rapidly with steam to liberate hydrogen.

$$Mg_{(s)} + H_2O_{(g)} \xrightarrow{100°C} MgO_{(s)} + H_{2(g)}$$

- **Calcium, strontium and barium** produce hydroxides with water.

$$M + 2H_2O \xrightarrow{100°C} M(OH)_2 + H_2$$

Q.5 Discuss the trends in chemical properties of compounds like oxides, hydroxides, carbonates, nitrates and sulphates of IA and IIA group elements.

General Trend in Properties of Compounds of Alkali and Alkaline Earth Metals

1. Oxides

Group IA oxides

Alkali metal oxides dissolve in water to give strongly alkaline solutions. For example:

$$Li_2O_{(s)} + H_2O_{(l)} \longrightarrow 2LiOH_{(aq)}$$

$$2Na_2O_{2(s)} + 2H_2O_{(l)} \longrightarrow 4NaOH_{(aq)} + O_{2(g)}$$

The reaction of an alkali metal oxide with water is an acid-base reaction and not an oxidation reduction reaction since no element undergoes a change in its oxidation number. The reaction simply involves the decomposition of water molecule by an oxide ion.

$$O^{2-} + H_2O \longrightarrow 2OH^-$$

Potassium super oxide (KO_2)

It has the ability to absorb carbon dioxide while giving out oxygen at the same time.

$$4KO_{2(s)} + 2CO_{2(g)} \longrightarrow 2K_2CO_{3(s)} + 3O_{2(g)}$$

That is why it has a very interesting use in breathing equipments for **mountaineers** and in space craft.

Group IIA Oxides

The solubility of alkaline earth metal oxides in water increases down the group. BeO and MgO are insoluble but CaO, SrO and BaO are soluble and react with water to form the corresponding hydroxides.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Basic character of oxides

The basic character of alkali metal oxides and alkaline earth metal oxides increases down the group. The tendency for group IIA oxides to form alkaline solution is relatively less than that of alkali metals.

Group I-A		Group II-A
Lithium oxide (Basic) Sodium oxide (Basic) Potassium oxide (Basic)	Increasing Basic character Decreasing Basic character	Beryllium oxide (Amphoteric) Magnesium oxide (Basic) Calcium oxide (Basic)

BeO is amphoteric in nature. Since it reacts with both acids and bases.

$$BeO + H_2SO_4 \longrightarrow BeSO_4 + H_2O$$

$$BeO + 2NaOH \longrightarrow \underset{\text{Sodium beryllate}}{Na_2BeO_2} + H_2O$$

2. Hydroxides

(a) Solubility of hydroxides

The alkali metal hydroxides are

- All crystalline solids.

IA Hydroxides	IIA Hydroxides
LiOH	$Be(OH)_2$
NaOH	$Mg(OH)_2$
KOH	$Ca(OH)_2$
RbOH	$Sr(OH)_2$
CsOH	$Ba(OH)_2$

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- Highly soluble in water except LiOH which is slightly soluble.
- Generally hygroscopic.
- Very strong bases, except LiOH.

The **solubility of alkaline earth metal hydroxides** in water increases down the group. $Be(OH)_2$ is quite insoluble, $Mg(OH)_2$ is sparingly soluble while $Ba(OH)_2$ is more soluble.

This increase in solubility is due to increase in the size of cations. Due to greater ionic radii of group IIA cations, the lattice energy of hydroxide decreases.

(b) Thermal stability

- Alkali metal hydroxides are stable to heat except LiOH, while alkaline earth metal hydroxides like $Mg(OH)_2$ and $Ca(OH)_2$ decompose on heating.

$$2LiOH_{(s)} \longrightarrow Li_2O_{(s)} + H_2O_{(\ell)}$$

$$Mg(OH)_{2(s)} \longrightarrow MgO_{(s)} + H_2O_{(\ell)}$$

Basic strength increases from LiOH to CsOH

Lime water: A saturated solution of $Ca(OH)_2$ in water is called Lime water. It is used as a test for CO_2.

Milk of Magnesia: A suspension of $Mg(OH)_2$ in water is called Milk of magnesia. It is used for treatment of acidity in stomach.

3. Carbonates

$$BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$$

Increasing ionic character and stability

(a) Carbonates of Alkali Metals

The carbonates of alkali metals are all soluble in water and are stable towards heat except Li_2CO_3 which is not only insoluble but also decompose on heating to lithium oxide.

$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$

The decomposition is made easy because the electrostatic attraction in converting from carbonate to oxide is considerable. In case of large cation like K^+ in K_2CO_3 (pearl ash), the gain in electrostatic attraction is relatively much less and the decomposition is difficult.

Sodium carbonate: It is very important industrial chemical. At temperature below 35.2°C, Na_2CO_3 crystallizes out from water as $Na_2CO_3.10H_2O$ which is called washing soda. Above this temperature it crystallizes out as $Na_2CO_3.H_2O$. On standing in air, $Na_2CO_3.10H_2O$ slowly loses water and converted to a white powder $Na_2CO_3.H_2O$.

Aqueous solution of Na_2CO_3 is basic in nature: The solution of Na_2CO_3 in water is basic due to hydrolysis of the carbonate ion.

$$Na_2CO_3 + 2H_2O \longrightarrow 2NaOH + H_2CO_3$$

(b) Carbonates of Alkaline Earth Metals

- Unlike the alkali metal carbonates, the alkaline earth metal carbonates are only very slightly soluble in water, with the solubility decreasing down the group.
- They also decompose on heating and the ease of decomposition decreases down the group.

$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$$

The case of decomposition can be related to the size of the metal ion, the smaller the ion, the more is the lattice energy of the resulting oxide and hence higher the stability of the product.

4. Nitrates

- Nitrates of both alkali and alkaline earth metals are soluble in water.
- Nitrates of Li, Mg, Ca and Ba decompose on heating to give O_2, NO_2 and the metallic oxide.

$$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$$

$$2Mg(NO_3)_2 \longrightarrow 2MgO + 4NO_2 + O_2$$

$$2Ca(NO_3)_2 \longrightarrow 2CaO + 4NO_2 + O_2$$

- The nitrates of Na and K decompose to give metal nitrite and O_2.

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

5. Sulphates

- All the **alkali metals sulphates** are soluble in water.
- The solubilities of **sulphates of alkaline earth metals**, gradually decrease down the group.
- $BeSO_4$ and $MgSO_4$ are fairly soluble in water. $CaSO_4$ is slightly soluble and $SrSO_4$ and $BaSO_4$ are almost insoluble.

Q7. (b) Why the aqueous solution of Na_2CO_3 is alkaline in nature?

Ans Sodium carbonate is formed by the reaction of sodium hydroxide (strong base) and carbonic acid (weak acid). When it is dissolved in water, it converts into sodium hydroxide and carbonic acid.

$$Na_2CO_3 + 2H_2O \longrightarrow H_2CO_3 + 2Na^+ + 2OH^-$$

NaOH is a strong base and is completely dissociated to give hydroxide ions. H_2CO_3 is a weak acid and is not completely dissociated. For this reason, solution of sodium carbonate in water is alkaline in nature.

11(b) Why lime water turns milky with CO_2 but becomes clear with excess of CO_2?

Ans When CO_2 is passed through lime water, calcium carbonate is formed which is insoluble in water, due to which lime water turns milky.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

When excess of CO_2 is passed through it, soluble calcium bicarbonate is formed. Thus the solution becomes clear.

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2 \quad \text{(water soluble)}$$

Gypsum

Calcium sulphate occurs in nature as gypsum $CaSO_4.2H_2O$. When it is gently heated above 100°C, it loses three quarters of its water of crystallization, giving a white powder called Plaster of Paris.

$$2CaSO_4.2H_2O \xrightarrow{120^\circ C} (CaSO_4)_2.H_2O + 3H_2O$$

Gypsum — Plaster of Paris

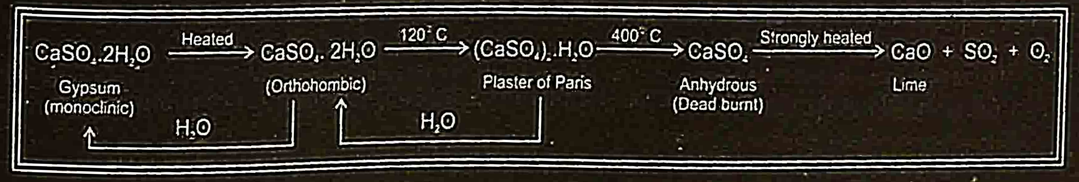
Q.11 (c) How gypsum is converted into plaster of Paris?

Ans Dihydrated calcium sulphate ($CaSO_4.2H_2O$) is called Gypsum, whereas half hydrated calcium sulphate ($CaSO_4.\frac{1}{2}H_2O$) is called plaster of Paris.

When gypsum is gently heated above 100°C, it loses three quarters of its water of crystallization and converts into Plaster of Paris.

$$2CaSO_4.2H_2O \xrightarrow{100^\circ C} (CaSO_4)_2.H_2O + 3H_2O$$

Gypsum — Plaster of Paris



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	Properties	Alkaline Earth Metals	Alkali Metals
(i)	Electronic configuration	Two electron are present in the valence shell. The configuration is ns^2.	One electron is present in the valence shell. The configuration is ns^1.
(ii)	Valency	Bivalent.	Monovalent.
(iii)	Electropositive nature	Less electropositive	More electropositive
(iv)	Hydroxides	Weak basis, less soluble and decompose on heating	Strong basis, highly soluble and stable towards heat.
(v)	Bicarbonates	These are not known in free state. Exist only in solution.	These are not known in solid state
(vi)	Carbonates	Insoluble in water. Decompose on heating.	Soluble in water. Do not decompose on heating (Li_2CO_3 is an exception).
(vii)	Action of nitrogen	Directly combine with nitrogen and form nitrides.	Do not directly combine with nitrogen except Li.
(viii)	Action of carbon	Directly combine with carbon and form carbides.	Do not directly combine with carbon except Li.
(ix)	Nitrates	Decompose on heating evolving a mixture of NO_2 and oxygen.	Decompose on heating evolving only oxygen.
(x)	Solubility of salts	Sulphates, phosphates, fluorides, chromates, oxalates, etc., are insoluble in water.	Sulphates, phosphates, fluorides, chromates, oxalates, etc., are soluble in water.
(xi)	Physical properties	Are less reactive and comparatively harder metals. High melting points. Diamagnetic	Soft, low melting points. Paramagnetic.
(xii)	Hydration of compounds	The compound are extensively hydrated. $MgCl_2.6H_2O$, $CaCl_2.6H_2O$ and $BaCl_2.2H_2O$ are hydrated chlorides.	The compound are less hydrated. NaCl, KCl and RbCl form non - hydrated chlorides
(xiii)	Reducing power	Weaker, as ionisation potential values are high and oxidation potential values are low	Stronger, as ionisation potential values are low and oxidation potential values are high.

Q.8 (a) Describe with diagram the manufacture of sodium by Down's cell.

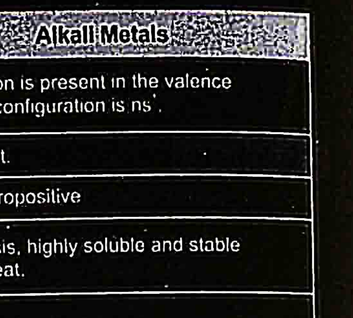
Commercial preparation of Sodium by Down's Cell

Objective

This cell is used for large scale preparation of Na metal.

Principle

Most of sodium metal is produced by the electrolysis of fused sodium chloride. Since the melting point of sodium chloride is 801°C, some calcium chloride is added to lower its melting point and to permit the furnace operate at about 600°C.



Down's cell

Construction and working

Anode: In the electrolytic cell, the large block of graphite at the centre is the anode above which there is a dome for the collection of chlorine.

Cathode: The cathode is a circular bar of copper or iron which surrounds the anode but is separated from it by an iron screen, which is terminated in a gauze.

The arrangement permits the electric current to pass freely but prevents sodium and chlorine from mixing after they have been set free at the electrodes. Sodium metal rises in a special compartment from which it is taken out at intervals.

Cell products: The cell produces dry chlorine and 99.9 percent pure sodium. The process is carried out at 600°C.

Reactions

When sodium chloride is heated at high temperature, it ionizes as follows:

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

Na^+ ions move towards cathode and Cl^- ions move towards anode.

At cathode $Na^+ + e^- \longrightarrow Na$ (Reduction)

At anode $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$ (Oxidation)

Net cell reaction $NaCl \longrightarrow Na + \frac{1}{2}Cl_2$

Q.8 (b) point out the three advantages of Down's cell process.

Advantages of Process

(a) The metallic fog is not produced.
(b) Liquid sodium can easily be collected at 600°C.
(c) Material of the cell is not attacked by the products formed during the electrolysis.

Q. Describe with diagram the manufacture of Caustic soda by diaphragm cell.

Commercial Preparation of Sodium Hydroxide by the Diaphragm Cell

Objective

This cell is used for large scale preparation of NaOH (Caustic Soda).

Principle

Sodium hydroxide is manufactured on a large scale by the electrolysis of aqueous solution of common salt in a diaphragm cell.

Construction and working:

- The cell is made up of steel tank. An oblong perforated steel vessel lined inside with asbestos diaphragm serves as a cathode.
- It is provided with a constant level device to keep the vessel filled to the specified level with brine.
- A graphite anode is held within the U-shape diaphragm and it projects into the salt solution.
- The steam is blown during the process which keeps the electrolyte warm and helps to keep the perforations clear.
- The chlorine released at the anode, rises into the dome at the top while hydrogen released at the cathode, escapes through a pipe. The sodium hydroxide solution slowly percholates into a catch basin.

Reaction at anode

When the electrolysis takes place, chlorine is given off at the anode according to the following reaction.

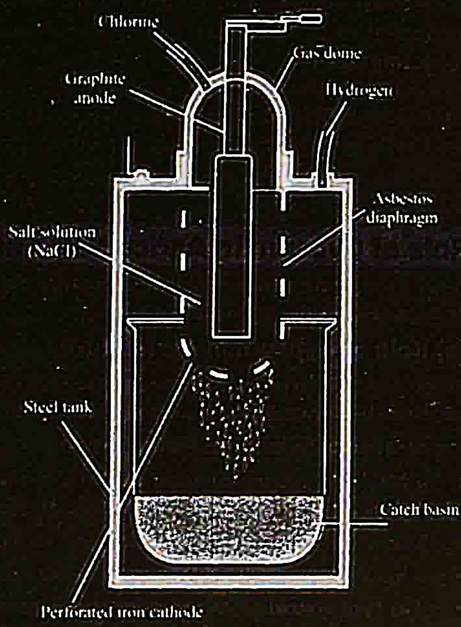
$$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e^-$$

Reaction at cathode:

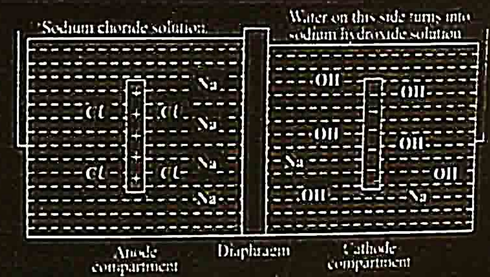
At the cathode, hydrogen is discharged by the reduction of water

$$2H_2O + 2e^- \longrightarrow 2OH^-_{(aq)} + H_{2(g)}$$

Sodium hydroxide, NaOH, is soft, waxy, white, corrosive solid. It is commonly known as lye or caustic soda.



Nelson cell for the production of NaOH.



The figure shows a simplified version of the cell in order to understand the purpose of diaphragm.

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The overall result of the above reactions is that the brine loses its chloride ions and the solution turns increasingly alkaline in cathode compartment.

Problems during working of cell

We can face two major problems during the working of the cell.

1. Chlorine produced can react with hydroxide ions in cold giving hypochlorite ions.

$$Cl_{2(g)} + 2OH^-_{(aq)} \longrightarrow OCl^-_{(aq)} + Cl^-_{(aq)} + H_2O$$

2. Hydroxide ions may be attracted towards anode, where they can be discharged releasing oxygen gas. This oxygen gas may contaminate the chlorine and renders it impure.

$$4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$$

Solution of Problems

1. **The first problem** is solved by using asbestos diaphragm. This keeps the two solutions separate while allowing sodium ions to move towards the cathode. This movement of ions keeps the current flowing through the external circuit.
2. **The second problem** is solved by keeping the level of brine in anode compartment slightly higher, this keeps the direction of flow of liquid towards the cathode and thus preventing the possibility of hydroxide ions to reach the anode.

Collecting NaOH

The solution that flows out of the cathode compartment contains 11% NaOH and 16% NaCl. Evaporation of this solution crystallizes the less soluble NaCl which is filtered off, the liquid left contains about 50% NaOH and only 1% NaCl as an impurity. For commercial purposes this small impurity is not important.

Role of Gypsum in Agriculture and Industry

Its chemical name is calcium sulphate di-hydrate and chemical formula is $CaSO_4.2H_2O$. It is a mineral that occurs in large deposits throughout the world.

(a) Role of Gypsum in Agriculture

Gypsum is applied to the soil as a **source of calcium and sulphur.** The calcium supplied by gypsum in fertilizers is of importance in crop production in area where soils are subject to extensive leaching.

Importance of Sulphur in Plant growth

- It has been recognized as an essential constituent of plants. For centuries, sulphur compounds had been applied to soils because of their observed beneficial effect on plant growth.
- It serves as a constituent of protein and various other compounds in plants.
- It has an influence on chlorophyll development in plant leaves. Plants deficient in sulphur exhibits a pale green colour.
- **The root system** of several plants has been observed to be greatly enlarged by the application of sulphur.

It has been reported that good crops are produced by the application of sulphur containing materials such as gypsum.

(b) Role of Gypsum in Industries

Gypsum

When gypsum is heated under carefully controlled conditions at 100°C, it loses three quarters of water of crystallization. The resulting product is called Plaster of Paris.

$$2[CaSO_4.2H_2O] \longrightarrow (CaSO_4)_2.H_2O + 3H_2O$$

Gypsum — Plaster of Paris

When gypsum is heated strongly at 400°C, it forms anhydrous salt which absorbs water slowly. Such plaster is called '**Dead burnt**'.

$$CaSO_4.2H_2O \longrightarrow CaSO_4 + 2H_2O$$

Gypsum — Dead burnt

Setting of Plaster of Paris

Plaster of Paris when mixed with half of its weight of water, it forms a plastic type viscous mass and then sets to a hard porous mass. This process is completed within **10 to 15 minutes.** During the process, expansion about **1 %** in volume also occurs, which fills the moulds completely and thus a **sharp impression** is achieved.

$$\underset{\text{Plaster of paris}}{(CaSO_4)_2.H_2O} \xrightarrow[H_2O]{\text{Setting}} \underset{\text{Orthohombic}}{CaSO_4.2H_2O} \xrightarrow{\text{Hardening}} \underset{\text{Monoclinic}}{CaSO_4.2H_2O}$$

Uses of Plaster of Paris

(i) It is used for making plaster walls, casts of statuary, coins, etc.
(ii) It is used in surgery, plaster of Paris bandages are used for holding in place fractured bones after they have been set.
(iii) Special plasters contain plaster of Paris and other ingredients which vary with the demands of the use to which they are to be put.

Varieties of Plasters

Two varieties of plasters are made.

(1) Cement Plaster

It is plaster of Paris to which usually **glue or other oils** have been added as retarders to **prolong the time of setting.**

(2) Hard finish Plasters

These are made by **the calcinations of the anhydrous sulphate with alum or borax.** These plasters are set very slowly but give a hard finish.

When mixed with wood pulp and allowed to set in the form of boards, it forms a material, much used in the construction of buildings as wall boards and partitions.

- Gypsum is also used as **filler in paper industry.**

Q11. (d) Why 2% gypsum is added in the cement?

Ans Portland cement is made by strongly heating a finely powdered mixture of clay and limestone. The final product, known as clinker, is cooled and then ground into a very fine powder. During the grinding there is added about 2% of gypsum which prevents the cement from hardening too rapidly. The addition of gypsum increases the setting time of cement.

Role of Lime in Agriculture and Industry

Lime, (CaO) is a soft, white compound which is obtained by the thermal decomposition of $CaCO_3$.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

(a) Role of lime in agriculture

Q.11 (e) Why lime is added to an acidic soil?

- Large quantities of calcium oxide (CaO) are used in agriculture for **neutralizing acidic soils.** It has been found that application of lime to acidic soils increases the amount of readily soluble phosphorus.
- Calcium oxide is used in large amounts for making **lime-sulphur sprays** which have a strong fungicidal action.

Slaking of lime

The hydroxide of calcium is obtained when the oxide of the calcium is allowed to react with water. The process is called **slaking of lime** and it is an exothermic reaction.

$$CaO + H_2O \longrightarrow Ca(OH)_2 \text{ (Slaked lime)}$$

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Functions of Calcium in Plant Growth

The presence of calcium is essential for the normal development of plants. The quantity of calcium required by different plants varies considerably. Its main functions are:

(i) An adequate supply of calcium appears to stimulate the **development of root hairs** and, in fact, the entire root system.

(ii) It is necessary for normal leave development and tends to accumulate in leaves as well as in bark.

(iii) An adequate supply of calcium is also essential for the optimum activity of micro-organisms that produce nitrates.

(iv) The effect of calcium on the supply of available phosphorus in the soil is of special significance. Soils containing sufficient calcium are slightly alkaline in nature.

- When a deficiency of calcium exists various substances such as aluminium (Al) and manganese (Mn) may accumulate in plants in harmful concentrations.

(b) Role of Lime in Industries

1. Large quantities of lime are used in the extraction and refining of metals.
2. Lime is also used in paper, cement and leather industries.

Q.11 (f) How lime and sand are used to make glass?

- The ability of lime to react with sand at high temperature forming calcium silicate ($CaSiO_3$) serves as an important basis for glass manufacture.

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

- Lime is used in ceramic industry for producing different types of sanitary materials.

Q.11 (g) How lime mortar is prepared?

Ans. **Ordinary mortar**, also called lime mortar, is prepared by mixing freshly slaked lime (one volume) with sand (three or four volumes) and water to form a thick paste. This material when placed between the stones and bricks hardens or sets, thus binding the blocks firmly together. The equations for the chemical reactions that take place when mortar hardens are:

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

$$Ca(OH)_2 + SiO_2 \longrightarrow CaSiO_3 + H_2O$$

6. Lime is also used in refining of sugar and other food products.
7. Lime is used in the manufacturing of bleaching powder, which is used for the bleaching of the fabric and paper pulp.

$$Ca(OH)_2 + Cl_2 \longrightarrow Ca(OCl)Cl + H_2O$$

8. A suspension of the calcium hydroxide $Ca(OH)_2$ is called **milk of lime** and is used as a white-wash.
9. When lime is heated with coke at about 2800°C in an electric furnace, calcium carbide is produced.

$$CaO + 3C \longrightarrow \underset{\text{calcium carbide}}{CaC_2} + CO$$

Calcium carbide on hydrolysis produces acetylene.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2 \text{ (acetylene)}$$

10. Lime is often employed as a **dehydrating agent**, for example, in the preparation of absolute alcohol and the drying of ammonia gas. A mixture of sodium hydroxide and calcium hydroxide (soda lime) is often employed to remove both water and carbon dioxide from certain gases.

KEY POINTS

1. The elements of group I-A except hydrogen are called 'Alkali metals' while those of group II-A are named as alkaline earth metals.
2. Alkali metals have only one electron in s-orbital of their valence shell. They lose one electron of the valence shell forming monovalent positive ions.
3. Alkaline earth metals have two electrons in s-orbital of their valence shell. They lose two electrons forming dipositive ions M^{++}.
4. Spodumene, petalite, halite, natron, alinite are the common minerals of alkali metals.
5. Beryl, magnesite, dolomite, epsom salt, asbestos, calcite, gypsum and barite are the important minerals of alkaline earth metals.
6. Lithium behaves different from the other alkali metals.
7. Lithium forms only normal oxide, whereas the other form higher oxides like peroxides and superoxides.
8. Beryllium is the only member of group II, which reacts with alkalies to give hydrogen. The other member do not react with alkalies.
9. Nitrides hydrolyse vigorously when treated with water, giving NH_3 and respective hydroxides.
10. Nitrates of lithium, magnesium and barium on heating give oxygen, nitrogen peroxide and the corresponding metallic oxides.
11. When gypsum is heated above 100°C, it loses three quarters of its water of crystallization, giving white powder of $CaSO_4.1/2\ H_2O$ which is called plaster of paris.
12. Sodium is prepared by the electrolysis of molten sodium chloride in Down's cell.
13. Calcium is necessary for development of leaves and it tends to accumulate in leaves and bark. An adequate quantity of calcium is essential for the optimum activity of microorganisms that produce nitrates.
14. Lime is used in paper and glass industries. It is also used for refining sugar products.

SOLVED OBJECTIVE EXERCISE

Q1. Fill in the blanks.

(i) Alkali metals are _____ reactive than alkaline – earth metals.

(ii) Alkali metals decompose water vigorously producing _____ and hydrogen.

(iii) When heated in a current of dry hydrogen, alkaline earth metals form white crystalline _____ of the type MH_2.

(iv) The beryllium hydroxide, like the hydroxide of aluminum is amphoteric, while the hydroxides of the other members of the group IIA are _____.

(v) The elements of the group IA are termed as alkali metals, because their _____ are alkaline.

(vi) Spodumene is an ore of _____ metal.

(vii) Alkali metal nitrates on heating give the corresponding _____ and oxygen.

(viii) $Na_2CO_3.H_2O$ is the chemical formula of a mineral of sodium which is known as _____.

(ix) Metallic bicarbonates are decomposed on heating into their carbonates, along with _____ and _____.

(x) Metal nitrates other than the alkali metals on heating decompose into the corresponding metal _____ along with the evolution of nitrogen peroxide and oxygen.

Answer Key.

(i)	More	(ii)	Metal hydroxide
(iii)	Metal hydrides	(iv)	Basic
(v)	Oxides/Solutions	(vi)	Lithium
(vii)	Nitrite	(viii)	Natron
(ix)	CO_2 & H_2O	(x)	Oxide

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Q2. Indicate True or False.

(i) Group IA elements are called alkali metals because their chlorides are alkaline in nature.
(ii) Alkali metals are very good conductor of electricity.
(iii) The hydroxides of alkali metals and alkaline – earth metals are soluble in water.
(iv) Plaster of Paris is hemihydrate.
(v) Alkali metals have low melting and boiling points as compared to those of alkaline – earth metals.
(vi) Lithium carbonate is decomposed to its oxide, but the carbonates of the other alkali metals are stable towards heat.
(vii) All alkali metal sulphates are insoluble in water
(viii) Lithium combines with nitrogen to from lithium nitride but other alkali metals do not react with nitrogen.
(ix) Trona is mineral of lithium.
(x) Alkaline – earth metals are stronger reducing agents than alkali metals.

Answer Key.

(i)	False	(ii)	True	(iii)	False	(iv)	False	(v)	True
(vi)	True	(vii)	False	(viii)	True	(ix)	False	(x)	False

Q3. Multiple Choice Questions. Encircle the correct answer.

(i) Which one of the following does not belong to alkaline-earth metals?
(a) Be (b) Ra (c) Ba (d) Rn

(ii) The oxides of beryllium are?
(a) Acidic (b) Basic (c) Amphoteric (d) None of these

(iii) Which ion will have maximum value of heat of hydration?
(a) Na^+ (b) Cs^{2+} (c) Ba^{2+} (d) Mg^{+2}

(iv) Which one of the following is not an alkali metal?
(a) Francium (b) Caesium (c) Rubidium (d) Radium

(v) Which of the following sulphates is not soluble in water?
(a) Sodium Sulphate (b) Potassium sulphate (c) Zinc sulphate (d) Barium sulphate

(vi) The element caesium bears resemblance with
(a) Ca (b) Cr (c) Both of these (d) None of these metals

(vii) Chile saltpetre has the chemical formula?
(a) $NaNO_3$ (b) KNO_2 (c) $Na_2B_4O_7$ (d) $Na_2CO_3.H_2O$

(viii) The mineral $CaSO_4.2H_2O$ has the general name:
(a) Gypsum (b) Dolomite (c) Calcite (d) Epsom salt

(ix) Down's cell is used to prepare?
(a) Sodium carbonate (b) Sodium bicarbonate (c) Sodium metal (d) Sodium hydroxide

(x) Which element is deposited at the cathode during the electrolysis of brine in diaphragm cell?
(a) H_2 (b) Na (c) Cl_2 (d) O_2

Solved Exercise MCQ's

No	Answer	Reason
(i)	(d) Rn	Rn is a noble gas.
(ii)	(c) Amphoteric	BeO is amphoteric because it behaves as an acid with bases and as a base with acids.
(iii)	(d) Mg^{+2}	Heat of hydration $\propto$ charge density $= \frac{\text{Charge}}{\text{Size}}$

(iv)	(d) Radium	Radium is an alkaline earth metal.
(v)	(d) Barium sulphate	Alkali metal sulphates are soluble in water. $ZnSO_4$ is also soluble.
(vi)	(d) None of these metals	Cs is alkali metal and bears resemblance with Li, Na, K, Rb & Fr.
(vii)	(a) $NaNO_3$	$NaNO_3$ is an important ore of Na.
(viii)	(a) Gypsum	Gypsum is important source of calcium.
(ix)	(c) Sodium metal	Down's cell is an electrolytic cell in which Na metal is extracted by the electrolysis of molten NaCl.
(x)	(a) H_2	$2H_2O + 2e \longrightarrow 2OH_{(aq)} + H_{2(g)}$ (Cathode)

Previous Board Questions

1. Write chemical formulas of: (a) Chile Salt Petre (b) Sylvite
2. Discuss the role of lime in Agriculture.
3. Why the solution of Na_2CO_3 in water is basic in nature?
4. Write names and formulas of two ores of Potassium.
5. What is milk of magnesia and give its uses?
6. Complete and balance following equation:
   (a) $BeO + NaOH \rightarrow$ (b) $CaO + C$
7. Give products and balance:
   (a) $KO_2 + CO_2 \rightarrow$ (b) $Mg_3N_2 + H_2 \rightarrow$
8. Give the trend of solubility of group. II A hydroxides in the periodic table with a reason.
9. What is clinker? Why 2% gypsum is added in the cement?
10. What is the function of calcium in plant growth?
11. Give reason how magnesium and calcium react with nitrogen to give nitrides which on hydrolysis give ammonia?
12. What do you mean by dead burnt?
13. Write down the chemical formula of (a) Sylvite (b) Chrysoberyl
14. Point out the three advantages of Down's cell.
15. How Lime Mortar is prepared?
16. Justify that BeO is an amphoteric oxide.
17. Give formulas of the minerals (a) Halite (b) Natron
18. Why lime water turns milky with CO_2 but becomes clear with excess of CO_2?
19. Give the reactions of BeO with acid and base.
20. Name the soluble sulphates of alkaline earth metals.
21. Mention three important raw materials for the manufacturing of cement.
22. Draw and label the diagram of Nelson cell.

For Answers study
Scholar's CHEMISTRY (Objective) XII
⇒ MCQ's ⇒ Entry Test MCQ's ⇒ MCQ's From Past Board Papers
⇒ Additional Short Questions with Answers
Previous Board papers and Many More in the Objective Chemistry

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CHAPTER 3

GROUP IIIA AND GROUP IVA ELEMENTS

Q14. Give the names, electronic configurations and occurrence of Group-IIIA elements of the periodic table.

Group IIIA Elements

The elements of group IIIA of the periodic table consists of boron, aluminium, gallium, indium and thallium.

Electronic configuration of group IIIA elements

Element	Symbol	At.Number	Electronic Configuration
Boron	B	5	$1s^2, 2s^2, 2p^1$
Aluminum	Al	13	$1s^2, 2s^2, 2p^6, 3s^2, 3p^1$
Gallium	Ga	31	$1s^2 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^1$
Indium	In	49	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^1$
Thallium	Tl	81	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^1$

- The small size and high nuclear charge make boron non-metallic while all the other elements of this group are metals. The abrupt increase in metallic character from B to Al is associated with the increased size of aluminium atom.
- The increase in the atomic size is not regular in this group. This is due to the presence of d electrons in heavier members which have poor shielding effect than s and p electrons.
- **Melting points** of group IIIA decrease downward in a group due to increase in the size of atoms but with few exceptions.
- **First ionization energy** decreases downward in group due to increased size of atom. However first IP value increases from Al to Ga due to the poor shielding of d-electron. First I.E. also shows abnormal behaviour from In to Tl due to the presence of f^{14}-electrons. By poor shielding, the force of attraction between nucleus and electronic cloud increases.

Physical Properties of Group IIIA Elements

Property	B	Al	Ga	In	Tl
Atomic Number	5	13	31	49	81
Density g/cm^3	2.33	2.7	5.93	7.3	11.85
Melting Points (°C)	2300	660	30	157	304
Boiling Points (°C)	2550	2467	2403	2080	1457
1st Ionization energy (kJ/mol)	801	577	579	558	589
Atomic Radius (pm)	80	125	126	144	148
Ionic Radius of 3+ ion (pm)	20	52	60	81	95
Electron affinity (kJ/mol)	–27	–45	–29	–29	–30
Electronegativity	2.0	1.5	1.6	1.7	1.8

Occurrence of Boron

- Boron is not an abundant element. It occurs in traces in most soils.

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- It has been found to be essential in very small amounts for the proper growth of many plants.
- Boron is always found in nature combined with oxygen, usually as oxyborate ions. Boron occurs principally as salts of various polyboric acids.

Name of Minerals of Boron	Chemical Formula
Borax or Tincal	$Na_2B_4O_7.10H_2O$
Colemanite	$Ca_2B_6O_{11}.5H_2O$
Orthoboric Acid	H_3BO_3 or $B(OH)_3$

The other elements of group IIIA gallium, indium and thallium are relatively rare and are obtained as by-products during the processing of other metals.

Q.15 Discuss the peculiar behaviour of boron with respect to the other members of Group-IIIA elements.

Peculiar Behaviour of Boron

Boron is the first member of the Group IIIA. It shows many dissimilarities with the members of its own group. The difference in the properties of boron and those of the other members of the series is mainly due to the large difference in their sizes and ionization energies.

1. Boron is the only element in Group IIIA which is non-metallic in behaviour.
2. It is the only element with less than four electrons in the outermost shell which is not a metal.
3. Boron always uses all the three of its valence electrons for bonding purposes and its common oxidation states are +3 and –3.
4. One of the outstanding features of the chemistry of boron is its ability to form molecular addition compounds.
5. Boron does not form ionic compounds with sulphate, nitrate or other anions because boron does not form a stable cation.

Compounds of Boron

Q16. (a) What is the borax?

Borax (Sodium Tetraborate, $Na_2B_4O_7.10H_2O$)

Borax is the sodium salt of tetraboric acid, $H_2B_4O_7$. It is most important of all borates. Its chemical name is sodium tetraborate decahydrate. (Boric acid is formed by NaOH (a strong base) and H_3BO_3 (a weak acid) so it is a basic salt.)

Occurrence of Borax

Borax occurs as a natural deposit called **tincal** in the dried up lakes of Tibet and California.

Q.16 (b) Describe commercial preparation of borax.

Manufacture of Borax

(i) From Soda ash

Formally borax was manufactured by treating a hot solution of boric acid with the proper amount of soda ash.

$$4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2$$

Boric acid — Borax

(ii) Colemanite

Now-a-days borax is almost exclusively obtained from calcium borate. Finely powdered colemanite is boiled with Na_2CO_3 solution. when $CaCO_3$ precipitates out and a mixture of borax and sodium metaborate is formed.

$$Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2$$

Colemanite

The clear solution from the top is taken off and is then allowed to crystallize, when crystals of borax separate out. To get more borax, CO_2 is blown through the mother-liquor, the sodium metaborate is decomposed into borax, which separates out in the form of fine crystals.

$$4NaBO_2 + CO_2 \longrightarrow Na_2CO_3 + Na_2B_4O_7$$

Sodium metaborate — Borax

(iii) From Tincal

Borax may also be obtained from tincal ($Na_2B_4O_7.10H_2O$).By treating tincal with water and subsequently evaporating the clear solution, when crystals of borax separate out.

Properties of Borax

Physical Properties

(i) Borax is a white crystalline solid.

(ii) It is sparingly soluble (very less soluble) in cold water but more soluble in hot water. In 100g of water at 10°C only 3g of borax is soluble but at 100°C its solubility is 99.3 grams.

(iii) If a saturated solution of borax be allowed to crystallize above 62°C, octahedral crystals of pentahydrate $Na_2B_4O_7.5H_2O$ separate out, but if temperature is below 62°C, decahydrate crystals $Na_2B_4O_7.10H_2O$ are formed.

Chemical Properties

1. Hydrolysis

Aqueous solution of borax is alkaline in nature due to hydrolysis.

$$Na_2B_4O_7 + 7H_2O \longrightarrow 2NaOH + 4H_3BO_3$$

Strong base — Weak acid

Aqueous solution of borax turns red litmus to blue due to the presence of alkali.

- Borax when dissolved in water ionizes as:

$$Na_2B_4O_7 \longrightarrow 2Na^+ + B_4O_7^{-2}$$

- Hydrolysis of $B_4O_7^{-2}$ ions occurs as follow:

$$B_4O_7^{-2} + 7H_2O \longrightarrow 4H_3BO_3 + 2OH^-$$

So a strong alkali (NaOH) is formed which is highly ionized. On the other hand, boric acid (H_3BO_3) is ionized to a little extent because it is a weak acid. Hence, **solution of borax as a whole is alkaline in nature.**

- Hydrolysis is prevented in the presence of glycerine.

2. Effect of Heat

When borax is heated, it loses water and swells up into a white porous mass due to the expulsion of water. On further heating it melts into a clear transparent glass, which dissolves many metallic oxides forming coloured beads. This reaction forms the basis of borax bead test.

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 2NaBO_2 + B_2O_3$$

Glassy mass

3. Reactions with Acids

Its aqueous solution reacts with HCl or H_2SO_4 to form boric acid:

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$$

Borax — Boric acid

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$$

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4. Reaction with Ammonium Chloride

When borax is heated with ammonium chloride boron nitride is produced.

$$Na_2B_4O_7 + 2NH_4Cl \longrightarrow 2NaCl + 2BN + B_2O_3 + 4H_2O$$

Q4. What is the action of an aqueous solution of borax on litmus?

Ans When borax is dissolved in water, it gives an alkaline solution due to hydrolysis.

$$Na_2B_4O_7 + 7H_2O \longrightarrow 2NaOH + 4H_3BO_3$$

Strong alkali Orthoboric acid

Since this aqueous solution of borax is alkaline in nature, so, turns red litmus blue.

Q.6 Explain the chemistry of borax bead test?

Borax Bead Test

Objective

This test is used as confirmatory test for coloured ions of the salt, i.e. Cu^{2+}, Fe^{+2}, Mn^{2+}, Co^{2+}, Cr^{3+}, Fe^{3+} and Ni^{2+}.

Procedure

Prepare a loop at the end of a platinum wire. Heat the wire and take a little powdered borax on the hot loop. Heat again, borax first swells up and then melts into colourless, glass-like beads on the loop.

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7$$

Anhydrous Borax (Swollen porous mass)

$$Na_2B_4O_7 \longrightarrow 2NaBO_2 + B_2O_3$$

Sod. metaborate boric anhydride

Now put a few grains of the substance, under examination, on the beads and re-heat it first in the oxidizing flame and then in the reducing flame.

Chemistry of Borax Bead Test

Borax, when fused, is decomposed into sodium metaborate and boric anhydride.

$$Na_2B_4O_7 \longrightarrow 2NaBO_2 + B_2O_3$$

The metallic oxide formed from the substance, under examination, combines with B_2O_3 giving the coloured metallic borates. With cupric oxide, the beads are coloured blue in the oxidizing flame because cupric borates are blue in colour.

$$CuSO_4 \longrightarrow CuO + SO_3$$

$$CuO + B_2O_3 \longrightarrow Cu(BO_2)_2$$

Metallic ion	Colour of beads in oxidizing flame	Colour of beads in reducing flame
Cu^{2+}	Bluish green	Red
Cr^{3+}	Green	Green
Co^{2+}	Blue	Blue
Ni^{2+}	Reddish brown	Black
Mn^{2+}	Violet	Colourless
Fe^{3+}	Yellow	Green

Q5. Give equations to represent the following reaction. (a) Borax is heated with CoO

Ans (a) When borax is heated it loses water of crystallization. It swells up into a white porous mass due to expulsion of water.

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10H_2O$$

Sod. tetraborate

When sodium tetraborate is fused, it decomposes into sod. Metaborate and boric anhydride.

$$Na_2B_4O_7 \longrightarrow 2NaBO_2 + B_2O_3$$ (Boric anhydride)

The cobalt oxide combines with B_2O_3 to give blue coloured cobalt meta borate, both in oxidizing and reducing flame.

$$CoO + B_2O_3 \longrightarrow Co(BO_2)_2$$ (Cobalt metaborate)

Q.16 (d) How does borax serve as a water softening agent?

Ans. The hardness of water is due to the presence of soluble salts of calcium and magnesium. When borax is treated with hard water, it can remove Ca^{2+} and Mg^{2+} ions from water as insoluble calcium tetra borate and Magnesium tetra borate respectively.

$$Ca^{2+} + Na_2B_4O_7 \longrightarrow CaB_4O_7 + 2Na$$

$$Mg^{2+} + Na_2B_4O_7 \longrightarrow MgB_4O_7 + 2Na$$

Q.16 (c) Outline the principal uses of borax.

Uses of Borax

1. It is used to prepare borate glass, which is heat resistant.
2. It is used in softening of water.
3. It is employed in borax bead test, for the detection of metallic cations.
4. It is used in metallurgical operations.
5. It is used as a flux in welding and in metallurgy.
6. It is employed in making washing powders.
7. It is used in leather industry for tanning and dyeing.
8. It is used in cosmetics, soaps, textiles, paints, medicine, and match industry and as a preservative.

Boric Acids

Q.12 Give the names and the formulas of different acids of boron?

There are four important boric acids. Out of these orthoboric acid is the most important and the stable one. The remaining acids are stable in solid state and change into orthoboric acid in solution:

(i) Orthoboric Acid, H_3BO_3 (ii) Metaboric Acid, HBO_2.
(iii) Tetraboric Acid, $H_2B_4O_7$ (iv) Pyroboric Acid, $H_4B_4O_9$

$$HBO_2 + H_2O \longrightarrow H_3BO_3$$

Metaboric acid Boric acid

$$H_2B_4O_7 + 5H_2O \longrightarrow 4H_3BO_3$$

Tetraboric acid Boric acid

Orthoboric Acid or Boric Acid (H_3BO_3)

It is well crystalline chemical substance (triclinic), sparingly soluble in cold water (2.6% at 40°C) but dissolves readily in hot water (37% at 107°C). This temperature variation in solubility forms the basis for its separation and purification.

Q.17 (b) How is boric acid prepared in laboratory?

Preparation of Boric Acid

1. From Colemanite

On commercial scale, boric acid is prepared from a natural calcium borate called colemanite ($Ca_2B_6O_{11}.5H_2O$) by suspending it in boiling water while, sulphur dioxide is passed through it. Boric acid crystallizes out from the solution while, the other product $CaSO_3$ remains in the solution.

$$Ca_2B_6O_{11}.5H_2O + 2SO_2 + 4H_2O \longrightarrow 2CaSO_3 + 6H_3BO_3$$

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2. From Borax

A hot concentrated solution of borax is treated with a calculated quantity of conc. H_2SO_4. On cooling, crystals of boric acid formed separate out.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$$

Borax — Boric acid

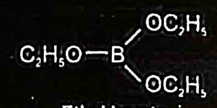
Q17.c Give properties of boric acid.

Q7.a How does orthoboric acid react with: (a) Sodium hydroxide (b) Ethyl alcohol

Properties of Boric Acid

1. Boric acid is a white lustrous crystalline solid having a soft soapy touch, very slightly soluble in cold water but fairly soluble in hot.
2. It is volatile in steam.
3. It reacts with ethyl alcohol, forming ethyl borate.

$$H_3BO_3 + 3C_2H_5OH \longrightarrow (C_2H_5)_3BO_3 + 3H_2O$$



Ethyl borato

4. When heated strongly, it swells to frothy mass losing water molecules. It is first converted into meta boric acid, then to tetra boric acid and finally to boric anhydride.

$$H_3BO_3 \xrightarrow{100°C} HBO_2 + H_2O$$

Metaboric Acid

$$4HBO_2 \xrightarrow{140°C} H_2B_4O_7 + H_2O$$

Tetraboric Acid

$$H_2B_4O_7 \xrightarrow{\text{Red hot}} 2B_2O_3 + H_2O$$

Boric anhydride

5. It is a very weak acid and ionizes to a very limited extent mainly as a mono basic acid.

$$H_3BO_3 + H_2O \longrightarrow [B(OH)_4]^- + H^+$$

6. Its solution has no effect on methyl orange, although it turns blue litmus red.
7. It is partially neutralized by caustic soda to give borax.

$$4H_3BO_3 + 2NaOH \longrightarrow Na_2B_4O_7 + 7H_2O$$

Borax

8. When boric acid is neutralized by soda ash (Na_2CO_3), borax is obtained.

$$4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2$$

9. Boric acid being a weak acid cannot be titrated with alkalies in the usual manner. In the presence of glycerol, however, it can be titrated against a standard alkali using phenolphthalein as an indicator. In the presence of glycerol, it acts as much stronger acid as compared to pure H_3BO_3.

Q8. How will you convert boric acid into borax and vice versa?

Ans **Conversion of Boric Acid into Borax:**

When boric acid is treated with caustic soda (NaOH) it gives borax.

$$4H_3BO_3 + 2NaOH \longrightarrow Na_2B_4O_7 + 7H_2O$$

Borax

Conversion of Borax into Boric acid:

When aqueous solution of borax reacts with HCl or H_2SO_4, it gives boric acid.

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3.$$

Boric Acid

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3.$$

Boric Acid

Q.17 (c) Give uses of boric acid.

Uses of Boric Acid

1. Boric acid is used in medicines as an antiseptic, e.g. dusting powder, boric ointment and boric solution is used as an eye-wash.
2. It is used in pottery as a glaze because borate glazes are more fusible than silicate glazes and possess a higher coefficient of expansion.
3. It is also used in candle industry for stiffening of wicks.

ALUMINIUM

Q.6 Why is aluminum not found as a free element?

Ans Aluminium is a reactive metal and does not exist in free state. It is mostly found in the form of alumino silicates and also as oxides.

Occurrence of Aluminium

- Aluminium is the third most abundant element in the earth's crust (after oxygen and silicon).
- It occurs primarily as alumino-silicate minerals found in the rocks of the outer portion of the earth.

Q.18 (a) Give the names along with the formulas of three important ores of aluminum.

Names of Minerals of Aluminium	Chemical Formula
Feldspar	$KAlSi_3O_8$ or $K_2O.Al_2O_3.6SiO_2$
Mica (Muiscovite)	$KH_2Al_3(SiO_4)_3$
Kaolin (Clay)	$H_2Al_2(SiO_4)_2.H_2O$ or $Al_2O_3.2SiO_2.2H_2O$
Corundum	Al_2O_3
Emerald	$Al_2F_2SiO_4$
Gibbsite	$Al_2O_3.3H_2O$ or $Al(OH)_3$
Bauxite	$Al_2O_3.2H_2O$
Cryolite	Na_3AlF_6
Diaspore	$Al_2O_3.H_2O$ or $AlO(OH)$

MCQ's
Which of the following is most abundant mineral of aluminium:
(a) Al_2O_3
(b) $Al_2O_3.H_2O$
(c) $Al_2O_3.2H_2O$
(d) All of these
Hint: Bauxite

Q.18 (b) How and under what conditions does aluminium react with the following
(i) Oxygen (ii) Hydrogen (iii) Halogens (iv) Acids (v) Alkalies

Reactions of Aluminium

(a) Reaction with Air

Q. Why aluminium is said to be corrosion-free?

Ans When a piece of aluminium sheet is exposed to moist air it acquires a thin, continuous coating of aluminium oxide, which prevents further attack on the metal by atmospheric oxygen and water under normal conditions. Because of this aluminium sheets are said to be corrosion-free.

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Heating of powdered aluminium at high temperature

If the aluminium powder is heated to 800°C and above, the metal will react with air to form aluminium oxide, Al_2O_3, and aluminium nitride, AlN. The reaction is accompanied by the evolution of heat and intense white light.

$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

$$2Al + N_2 \longrightarrow 2AlN$$

Utilization

(i) Since the reaction is highly exothermic so used in thermite process.
(ii) This property of aluminium is made use of in flash light photography.
(iii) Because of its ability to combine with both oxygen and nitrogen, the metal is often used to remove air bubbles from molten metals.

Caution: Salt solutions corrode aluminium badly so aluminium and aluminium alloys are not suitable for marine use.

(b) Reaction with Non-Metals

Heated aluminium combines with the halogens, sulphur, nitrogen, phosphorus and carbon, accompanied by the evolution of heat.

$$2Al_{(s)} + 3Cl_{2(g)} \longrightarrow 2AlCl_{3(s)}$$

Aluminium on heating with hydrogen forms aluminium hydride.

$$2Al + 3H_2 \xrightarrow{\text{Heat}} 2AlH_3$$

(c) Reaction with Acids

Aluminium is amphoteric. It dissolves in both acids and bases with the liberation of hydrogen gas.

(i) With HCl

Aluminium reacts slowly with dilute acid and more rapidly with concentrated hydrochloric acid to displace hydrogen.

$$2Al_{(s)} + 6HCl_{(aq)} \longrightarrow 2AlCl_{3(aq)} + 3H_{2(g)}$$

(ii) With H_2SO_4

Aluminium does not react with dilute sulphuric acid. However, it is oxidized by hot concentrated sulphuric acid to liberate sulphur dioxide gas.

$$2Al_{(s)} + 6H_2SO_{4(aq)} \longrightarrow Al_2(SO_4)_{3(aq)} + 3SO_{2(g)} + 6H_2O_{(\ell)}$$

(iii) With HNO_3

Aluminium does not react with nitric acid at any concentration, probably because of the formation of protective layer of aluminium oxide. The acid is said to render the aluminium passive. Nitric acid is, therefore, frequently transported in aluminium containers.

(d) Reaction with alkalies

Aluminium dissolves in both sodium and potassium hydroxides to form a soluble aluminate, with the evolution of hydrogen.

$$2Al_{(s)} + 2NaOH_{(aq)} + 6H_2O_{(\ell)} \longrightarrow 2NaAl(OH)_{4(aq)} + 3H_{2(g)}$$

Uses of Aluminium

1. Aluminium is very light metal (nearly three times less dense than iron) but possesses high tensile strength. These properties account for its extensive use in the transport industries, in the construction of aircrafts, ships and cars.
2. It is an excellent conductor of heat and electricity. Thus, it is used as heat exchanger in chemical, oil and other industries. Heavy duty electrical cables are made of aluminium metal.
3. Aluminium is an excellent reflector of radiant energy. For this reason it is commonly used to insulate buildings. Aluminium foil is also used to jam radar.
4. It is non-magnetic and is thus used in **navigational equipments.**
5. It is a good reducing agent and can thus be used for this purpose in the chemical and steel industry.
6. It is nontoxic and can be used for making food and brewing equipments and in packaging.

7. Aluminium readily forms alloys with other metals like copper, magnesium, nickel and zinc.
8. At homes, aluminium is found in the form of cooking utensils, window frames and kitchen foil.
9. Aluminium is used for making petrol and milk storage tanks because it reflects heat and prevents them of being over-heated in the sun.

GROUP IVA ELEMENTS

Q.19 Give the names, electronic configurations and occurrence of Group-IVA elements of the periodic table.

Elements of group IVA consist of carbon, silicon, germanium, tin and lead.

There is a marked change of properties from carbon to lead. This gradation is of such nature, however, that there are very few similarities between the extreme members. Thus carbon and lead differ very considerably; for more, for example, than do lithium and caesium in group IA.

The electronic configuration of group IVA elements.

Elements	Symbol	At. Number	Electronic Configuration
Carbon	C	6	$1s^2, 2s^2, 2p^2$
Silicon	Si	14	$1s^2, 2s^2, 2p^6, 3s^2, 3p^2$
Germanium	Ge	32	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^2$.
Tin	Sn	50	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^2$
Lead	Pb	82	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^2$

Electronic Configuration and Physical Properties of Group IVA Elements

Property	C	Si	Ge	Sn	Pb
Atomic Number	6	14	32	50	82
Electronic configuration	$[He]2s^22p^2$	$[Ne]3s^23p^2$	$[Ar]3d^{10}4s^24p^2$	$[Kr]4d^{10}5s^25p^2$	$[Xe]4f^{14}5d^{10}6s^26p^2$
Ionization energy (kJ/mol)	1086	736	760	707	715
Electron affinity (kJ/mol)	-122.5	-120	-116	-121	-101
Electronegativity	2.5	1.8	1.8	1.8	1.8
Atomic radius(pm)	77	117	122	140	154
Ionic radius of 2+ ion (pm)	60	71	73	93	121
Melting points (°C)	3570	1410	937	232	328
Boiling points (°C)	Sublimes	2355	2830	2270	1750
Density (g/cm^3)	2.33	2.7	5.93	7.3	11.85

Some common properties of carbon

Carbon and silicon are the only non metal in group IVA.

Metallic character

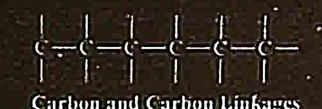
The electropositive character increases from carbon to lead which increases the metallic character of the elements. Thus carbon and silicon are the only non-metals in group IVA.

Catenation

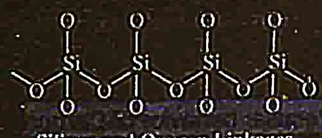
Carbon has the peculiar property of forming long carbon chains, silicon forms long chains of alternating silicon and oxygen atoms.

Nature of oxides

Carbon and silicon both form acidic oxides, whereas the oxides of germanium, tin and lead are amphoteric in nature.



Carbon and Carbon Linkages



Silicon and Oxygen Linkages

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Nature of boding

Both carbon and silicon form covalent bonds. Their oxides are acidic and both form hydrides and chloride.

Q. What do you mean by inert pair effect?

Ans **Inert Pair:** The pair of outermost electrons that does not readily take part in chemical combination is termed as inert pair and its effect is termed as inert pair effect.

Explanation

The elements of group IVA are characterized by a set of four valence electrons which form two pairs.
In the first three elements of IVA group, carbon silicon and germanium, all the four outermost electrons are used as valence electrons, while in tin and lead either all four (stannic and plumbic compounds) or only one of the pairs of electrons (stannous and plumbous compound) is used for bonding.

Common properties of the elements of Group IVA

1. All the elements of this group show a valency of four e.g., CO_2, SiO_2, $PbCl_4$ etc.
2. All of them form hydrides, MH_4 e.g., methane CH_4, Silane SiH_4, Germane GeH_4 etc.
3. They form tetrachlorides, MCl_4 e.g., CCl_4, $SiCl_4$, $GeCl_4$ $SnCl_4$, $PbCl_4$.
4. They also form the dioxides, MO_2 e.g., CO_2, SiO_2, GeO_2, SnO_2, and PbO_2.

Occurrence of Carbon

Carbon occurs naturally in two states.

(i) Crystalline (Graphite, diamond) form

(ii) Amorphous (Coal, Charcoal) form

Minerals of Carbon	Chemical Formula
Limestone (calcite)	$CaCO_3$
Dolomite	$MgCO_3 \cdot CaCO_3$
Magnesite	$MgCO_3$

Occurrence of Silicon

Minerals of Silicon	Chemical Formula
Analcite (a zeolite)	$NaAl(SiO_3)_2 . H_2O$
Asbestos	$CaMg_3(SiO_3)_4$
Kaolin (pottery clay)	$H_2Al_2(SiO_4)_2 . H_2O$
Zircon	$ZrSiO_4$
Talc (or soapstone)	$H_2Mg_3(SiO_3)_4$

- Silicon is very abundant, about 25% of the mass of the earth's crust being due to this element.
- Silicon, unlike carbon, is not found in free state.
- Silicon is found as a major constituent of rocks either in the form of silica or silicates.
- Most minerals other than sulphides, sulphates, phosphates and carbonates contains a high proportions of silicon.
- As oxide, it is found as quartz in the following forms:
  Rock crystal, amethyst, quartz, smoky quartz, rose quartz and milky quartz.
- Sand is largely silicon dioxide (silica).
- Opal is a hydrated variety of quartz.

Q. Discuss the peculiar behavior of carbon with respect to the other members of IVA group.

Peculiar behavior of Carbon

Carbon differs from the remaining members of Group IV-A in the following respects:

1. Metallic Characters:

Carbon and silicon are non-metals while the other members of the family are metalloids or metals.

2. Catenation or self-linkage:

Carbon has a tendency to form long chains of identical atoms. The type of linkage of identical atoms with each other is called catenation or self-linkage. The property of catenation decreases on moving down the group from carbon to lead. The maximum tendency of catenation associated with carbon forms the basis of the carbon compounds which constitute organic chemistry.

Compounds of Carbon and Silicon

Structure of Oxides of Carbon

Three oxides of carbon are known:

(i) Carbon monoxide, CO (ii) Carbon dioxide, CO_2 (iii) Carbon suboxide, C_3O_2

Out of these, the last one is of little importance.

Structure of Carbon Monoxide

Carbon monoxide is diatomic molecule having triple bond between the two atoms. It is very slightly polar. The electronic structure of carbon monoxide can be represented as:

$$:C::O:$$

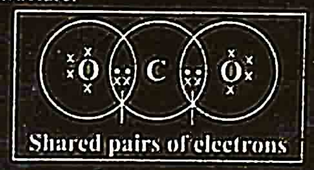
It is usually written as: $:C\equiv O:$

It might appear from the above structure that the molecule should have a large dipole moment, but in fact the molecule has a small dipole moment (0.112D).

$$^{\delta-}C \rightleftharpoons O^{\delta+}$$

Structure of Carbon Dioxide

In Gaseous State: Carbon dioxide exists in the gaseous state as linear molecule. The observed C–O bond distance is 115 pm and is in agreement with the following structure.



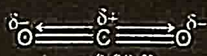
Shared pairs of electrons

In Solid State: Solid CO_2 (dry ice) has a face-centered cubic structure. Being linear, its dipole moment is zero.

Q10. Explain: (a) CO_2 is non – polar in nature. (b) CO_2 is acidic in character.

Ans **(a) Non-Polar Nature of CO_2:**

CO_2 has a linear structure.



$\mu = 0.00$ D

In CO_2 the central carbon atom is sp hybridized and there is no lone pair of electrons on it. The individual dipoles being same in magnitude but opposite in direction cancel the effect of each other's, therefore dipole moment of CO_2 is Zero.

(b) Acidic Character of CO_2:

CO_2 is a non-metal oxide. When it is dissolved in water, carbonic acid is formed.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

Due to H_2CO_3 formation, it is acidic in nature.

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Oxides of Silicon

Silicon Dioxide (SiO_2)

Silicon dioxide, SiO_2 called silica, is probably the most common and the most important compound of silicon. In silica every silicon atom is attached tetrahedrally to four oxygen atoms and each oxygen atom have two close silicon neighbours.

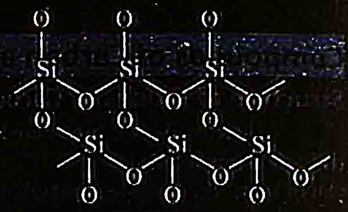
Quartz

Quartz is the common crystalline form of silicon dioxide. It is a hard, brittle, refractor, colourless solid which differs very markedly from carbon dioxide.

Structure of Silica

Tetrahedral Structure

In the interior of the silica network every silicon atom is bonded tetrahedrally to four oxygen atoms and every oxygen atom is bonded to two silicon atoms. The overall ratio of silicon to oxygen atoms is 1:2 and the simplest formula for silica therefore is SiO_2. The silicon oxygen bonds are strong and keep the atoms firmly in place.



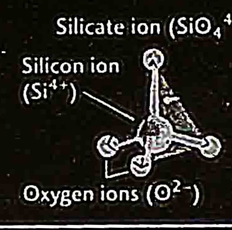
Structure of silicon dioxide

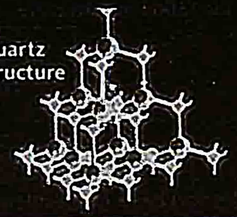
Giant molecule

SiO_2 is not the molecular formula for silica but the whole chunk of silica must be considered to be essentially one molecule. The atoms of silicon and oxygen at the surface of the chunk do not have all their valence forces satisfied, as is shown by the high surface activity of silica.

Crystalline forms of silica

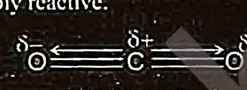
In each of the various crystalline forms of silica, there is a special pattern which is repeated throughout the crystal in a regular definite crystal lattice. The regular tetrahedral arrangement of four oxygen atoms around each silicon persists in each crystalline form but the Si-O-Si bond angles and the rotation about each Si-O bond are different in the different polymorphic species.



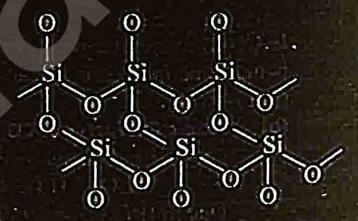


Q. Why is CO_2 a gas at room temperature while SiO_2 is a solid?

Ans CO_2 molecule has a monomeric linear structure while SiO_2 has an infinite three dimensional polymeric tetrahedral structure. The reason is that size of carbon atom is smaller than size of silicon atom. So, in CO_2 each carbon atom forms two double bonds with two oxygen atoms. In this way a small, symmetrical, linear molecule of CO_2 is formed, which is volatile and reasonably reactive.



In case of SiO_2, each silicon atom because of its large size is covalently bonded with four oxygen atoms and each oxygen atom is attached with two silicon atoms. In this way a three dimensional network is formed. So giant structure of SiO_2 is very stable. Thus SiO_2 exists as solid.



Structure of silicon dioxide

Vitreous Silica or Silica Glass

Preparation

When crystalline silica is heated sufficiently (1600°C) it melts to give a viscous liquid having a random structure, presumably with the silicon atoms still on the average close to four oxygen atoms and the oxygen atoms close to two silicon atoms. When this liquid silica is cooled it does not crystallize readily, but usually it undercools tremendously and eventually becomes rigid without having undergone orientation into a regular crystal pattern. This rigid, highly undercooled liquid is called vitreous silica or silica glass (frequently incorrectly referred to as fused quartz).

Properties

Vitreous silica possesses the following interesting and useful properties:

1. High transparency to light.
2. Very refractory (heat resistant), does not soften below 1500 to 1600°C.
3. Very low thermal expansion. (Not easily fractured by changing temperature)
4. Excellent insulator.
5. Hard, brittle, and elastic.
6. Insoluble in water and inert toward many reagents.
7. It is resistance towards all acids except HF.

Silicates and their uses

The compounds derived from silicic acid (H_2SiO_3) are termed as silicates.

(i) Sodium Silicate (Na_2SiO_3)

This is a sodium salt of meta-silicic acid H_2SiO_3. It is known water glass or soluble glass. It is prepared by fusing sodium carbonate with pure sand. The process is carried out in a furnace called **reverberatory** furnace.

$$Na_2CO_3 + SiO_2 \longrightarrow \underset{\text{sodium silicate}}{Na_2SiO_3} + CO_2$$

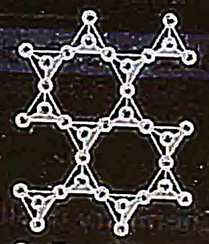
Properties

Sodium silicate is soluble in water and its solution is strongly alkaline due to the hydrolysis.

$$Na_2SiO_3 + 2H_2O \longrightarrow 2NaOH + H_2SiO_3$$

Uses of sodium silicate

(i) It is used as a filler for soap in soap industry.
(ii) It is used in textile as a fire proof.
(iii) It is used as furniture polish.
(iv) It is also used in calico printing.



Sodium Silicate

Chemical Garden

When crystals of soluble coloured salt like nickel chloride, ferrous sulphate, copper sulphate or cobalt nitrate, etc. are placed in a solution of sodium silicate, they produce a very beautiful growth, like plant, which is called chemical garden.

(ii) Aluminium Silicates

Weathering of Silicate Rocks

Aluminium silicates are formed by the chemical weathering of the rocks. Clay is an example of aluminium silicate. Clay is formed by disintegration and weathering of rocks.

The melting and freezing of water in the rocks and the chemical action of water and carbon dioxide, convert these compounds into potassium carbonate, sand and clay. The following reaction explains the weathering of potassium Feldspar

$$\underset{\text{Feldspar}}{K_2O.Al_2O_3.6SiO_2} + H_2CO_3 + H_2O \longrightarrow K_2CO_3 + 4SiO_2 + \underset{\text{Clay}}{Al_2O_3.(SiO_2)_2.2H_2O}$$

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Pure Clay

- Pure clay which has the formula shown above, is white and is called kaolin.
- It is used to make porcelain and china wares.
- Ordinary clay contains compounds of iron and other metals and it has a yellow or reddish yellow colour.

Impure clays

Impure clays can be more easily fused because they contain oxides of iron, calcium, magnesium and other metals which form easily fusible silicates with sand.

Uses: Such clays are used to make bricks, tiles and stonewares.

- **Due to the presence of ferric oxide, the articles of this clay turn reddish when heated in a kiln.**

Glazing of stoneware

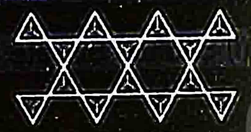
Stoneware is usually glazed to give a less porous surface by throwing salt upon the articles while they are hot. This treatment produces sodium aluminate $NaAlO_2$ and sodium aluminum silicate, which melt readily and cover the entire surface. When the article cools, the covering solidifies, producing a compact, smooth waterproof surface. China wares are made from a mixture of kaolin, bone ash, and feldspar; the mixture fuses when heated and fills the pores between the grains of kaolin.

Hardening of Clay

The use of clay in making pottery and other ceramic articles depends upon the plasticity of the paste. When soaked in water, the clay progressively hydrates, and the paste becomes more plastic. When the clay is heated, the water of hydration is lost, and a hard rock like mass is formed.

Talc or Soapstone (Magnesium silicate)

- The magnesium silicate $Mg_3H_2(SiO_3)_4$ is commonly known as talc or soapstone.
- It is physically greasy to touch.
- It is used in making cosmetics.
- It is also used in making house hold articles.



Asbestos (Calcium magnesium silicate)

- Asbestos is hydrate calcium magnesium silicate $CaMg_3(SiO_3)_4$.
- It is commonly used in making incombustible fabrics and hardboard etc.

Chemistry of Silicon and Carbon

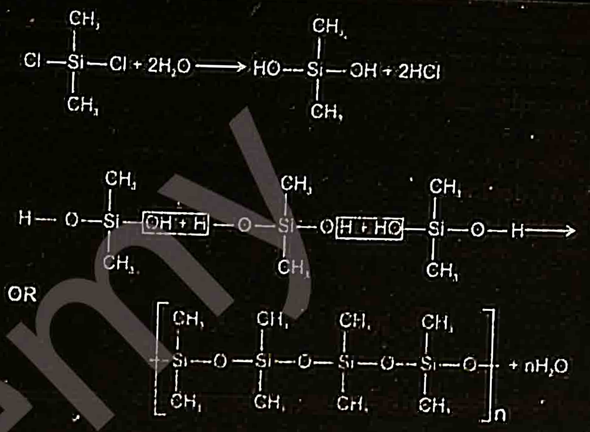
The chemistry of silicon is, in many respects, very much like the chemistry of carbon. Just as carbon forms the compounds carbon dioxide (CO_2), carbon tetrachloride (CCl_4), and methane (CH_4), similarly silicon forms silicon dioxide (SiO_2), silicon tetrachloride ($SiCl_4$), and silane (SiH_4). The silicon atom holds four methyl groups, $Si(CH_3)_4$, just as the carbon atom, $C(CH_3)_4$.

Silicones

"An organo silicon polymer in which Si – O – Si chain is present having alkyl or aryl groups attached to the Si – atom are called silicones."

Preparation

If a compound of silicon containing chlorine atoms and methyl groups, $SiCl_2(CH_3)_2$, is allowed to react with water, hydrogen chloride (HCl) comes out and the silicon atoms join together through oxygen atoms.



By this reaction we can make synthetically the silicon oxygen chains found in the mineral silicates. A difference is that there we have – CH_3 groups instead of oxygen atoms joined to silicon as side chains. Such a compound is called a silicone; this particular one is a methyl silicone. Other alkyl groups may also be substituted for the methyl groups and the molecular chain can be made of various lengths.

Properties

(i) Low molecular mass silicones are oily liquids. While high molecular mass silicones are waxy solids or rubber like solids.
(ii) Chemical reagent has no effect on them.
(iii) They are stable towards heat.
(iv) They are non-toxic.
(v) Small change in viscosity with the change in temperature.
(vi) They are excellent insulators.
(vii) They are water repellent.

Uses of Silicones

1. As lubricants

Some of the methyl silicones are oily liquids and they become more viscous as the chain length increases. They are used as lubricants, either incorporated in greases or as oils, in bearings, gears etc. They are also used in hydraulic breaks and other hydraulic systems. The outstanding physical attribute of silicone oil is its very small change in viscosity with change in temperature, compared with the behaviour of other oils of similar viscosity.

If the temperature is dropped from 100°C to 0°C the viscosity of petroleum oil may increase about one hundred folds, whereas that of silicone oil will increase less than four folds. In the presence of air or oxygen at temperature as high as 300°C, silicone oils remain free from acid formation, oxidation and similar phenomena, which frequently limit the usefulness of petroleum products and other synthetic organic liquids.

2. As rubber

Methyl silicones of high molecular mass resemble rubber and are used in making rubber like tubing and sheets.

3. As insulators

Silicone molecules can be made in such a way that bridges or cross linkages bind one long molecule to another at several points along the chain. These compounds have resinous properties and are extensively used in electrical insulation.

4. As water repellents

Another interesting and important application of silicones is their use in the treatment of various surfaces to make them water repellent. A silicone film covers the surface, and repels water like a grease film. Much of the leak of electricity through moisture film on ceramic electrical insulators can be prevented by a silicone film; cloth, plastics, asbestos, glass, leather, and paper, even filter paper and blotting paper become strongly water repellent when covered with silicone film.

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Q.9 Why are liquids silicones preferred over ordinary organic lubricants.

Ans

Small change in viscosity with temperature

If the temperature is dropped from 100°C to 0°C the viscosity of petroleum oil may increase about one hundred folds, whereas that of silicone oil will increase less than four folds.

Resistant towards oxidation

In the presence of air or oxygen at temperature as high as 300°C, silicone oils remain free from acid formation, oxidation and similar phenomena, which frequently limit the usefulness of petroleum products and other synthetic organic liquids.

Semiconductors

Q. What is a semi-conductor?

Ans A substance that has different resistances to the passage of an electric current under different circumstances is called a semi-conductor.

Q. Why a semi-conductor is called so?

Ans A semi-conductor conducts electricity better than an insulator but not as well as good conductors like metals. So they are also called half-conductors.

Q. What is the effect of heat and light on the conductivity of a semi-conductor?

Ans **Conductivity of a semi-conductor:** The electrons of semi-conductors do not carry electric current as readily as the electrons of metals which are good conductors. However, when the atoms of semi-conductor absorb heat or light, the electrons become less tightly bound to their atoms and conductivity increases.

Effect of Temperature

Contrary to the metals, the electrical conductivity of a semi-conductor increases by increasing the temperature.

Effect of Light

Semi-conductors are sensitive to light. The greater the intensity of light that shines on them, the better they conduct electricity. Due to this semi-conductors are used in photo-electric cells and in solar batteries.

Q. Inlist the elements or compounds commonly used as semi-conductors.

Ans Some common semiconductor materials are given below in the table:

Elements	Compounds
Si (Silicon)	Lead sulphide
Ge (Germanium)	Silicon carbide
Se (Selenium)	Cadmium sulphide
	Lead telluride
	Gallium arsenide
	Indium antimonide

Q. Semi-conductors are used as transistors.

Ans Another special property of semiconductors is the way they behave when they are joined to another material, which may be a metal or a different semiconductor. The junction between the different materials forms a boundary. It allows electricity to pass more properly and is used in transistors. Transistors are much smaller and less complicated than old fashioned electronic tubes. They are used in radio, television, computers and calculators.

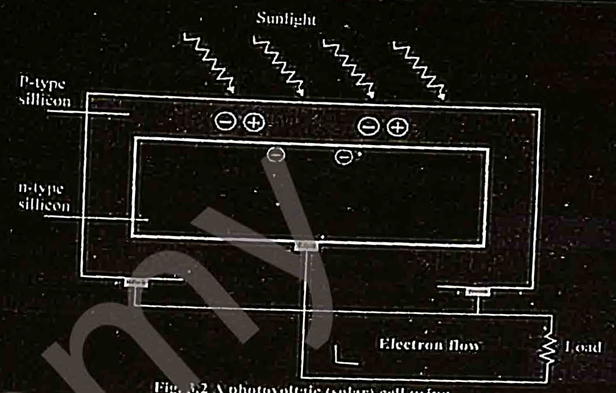


Fig. 3.2 A photovoltaic (solar) cell using silicon-based semiconductors

Q.13 What is the importance of oxides of lead in paints?

Uses of Lead Compounds in Paints

Various oxides of lead, basic lead carbonate and lead chromate are commonly used as pigments in paints.

1. Lead Suboxide (Pb_2O)

It is a black powder, obtained on heating plumbous oxalate in the absence of air

$$2PbC_2O_4 \xrightarrow{Heat} Pb_2O + 3CO_2 + CO$$

Pb_2O is decomposed by heat into Pb and PbO. Other than pigment, it is also used in the manufacture of lead storage batteries.

2. Lead monoxide (Litharge, Massicot), PbO:

Litharge varies in colour from pale yellow to reddish yellow, possibly owing to the existence of two forms, a rhombic (yellow) and a tetragonal (red). It is slightly soluble in water.

Uses of lead monoxide:

(i) It is usually used in preparing flint glass and paints.

(ii) If litharge is boiled with water and olive oil, lead oleate which is a sticky adhesive mass is formed and glycerin passes into solution.

(iii) It is used in preparing oils and varnishes.

3. Triplumbic Tetra oxide (Red lead or minium (Sindhur) Pb_3O_4

Preparation:

When lead is heated in air at about 340°C, it absorbs oxygen and forms a bright scarlet crystalline powder of red lead or **minium.**

$$3Pb + 2O_2 \longrightarrow \underset{\text{Triplumbic tetraoxide}}{Pb_3O_4}$$

It decomposes at 470°C

$$2Pb_3O_4 \xrightarrow{470\,C} 6PbO + O_2$$

Uses:

Red lead is used for a variety of purposes as:

(i) It is used for manufacture of lead storage batteries.

(ii) It is used as pigment in paints applied to steel and iron to retard corrosion.

(iii) It is an important ingredient for the manufacture of flint glass, matches and ceramic glazes.

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4. Lead Dioxide (PbO_2)

When red lead is treated with concentrated nitric acid, it is decomposed into lead nitrate and lead dioxide:

$$Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$

- Lead dioxide is a reddish brown powder.
- It is not very soluble in water, but it does dissolve in alkaline water to yield soluble plumbates.
- It is not affected by dilute acids.

5. White lead $2PbCO_3.Pb(OH)_2$

Basic lead carbonate $2PbCO_3.Pb(OH)_2$ is an amorphous white pigment. It mixes readily with linseed oil and has a good covering power. If improperly prepared, it becomes crystalline and its covering power is reduced.

White lead is not suitable for use as a good pigment since it is darkened by the hydrogen sulphide, which is frequently present in the atmosphere.

6. Lead chromate ($PbCrO_4$)

It is used as a pigment under the name of **chrome yellow**. Orange or red basic lead chromates are formed when lead chromate is boiled with dilute alkali hydroxide and are used as pigments. The stable yellow modification of lead chromate is monoclinic. Mixture of lead chromate with lead sulphate or barium sulphate are also used as yellow pigments.

KEY POINTS

1. Boron occurs in traces and has been found to be important for the growth of many plants.
2. Borax ($Na_2B_4O_7.10H_2O$), Colemanite ($Ca_2B_6O_{11}.5H_2O$), Orthoboric acid (H_3BO_3) are the common minerals of boron.
3. Aluminium, after oxygen and silicon, is the third most abundant element in the earth's crust. Feldspar ($K_2O.Al_2O_3.6SiO_2$), Corundum (Al_2O_3), Bauxite ($Al_2O_3.2H_2O$) and Cryolite (Na_3AlF_6) are the common minerals of aluminium.
4. The pair of outermost electrons that does not readily take part in chemical combination is termed as inert pair.
5. When heated, borax fuses, loses water of crystallization and swells up into a white porous mass. It is employed in borax bead test for identification of coloured salts.
6. When a hot concentrated solution of borax is treated with a calculated quantity of conc. H_2SO_4, On cooling, crystals of boric acid are produced.
7. When aluminium is burnt in oxygen a brilliant light is produced.
8. The electronic configuration of group IV-A elements shows that they have four electrons in their valence shells, two electrons of which are in s-orbital and the remaining two are in p-orbitals.
9. Limestone, dolomite and magnesite are the common minerals of carbon.
10. Feldspar, potash, mica and zircon are the famous minerals of silicon.
11. Silica has a network structure in which every silicon atom is bonded tetrahedrally to four oxygen atoms and every oxygen atom is bonded to two silicon atoms.
12. Sodium silicate, aluminium silicate, talc and asbestos are commercially important compounds of silicon and oxygen called silicates.
13. Methyl silicones can be used as lubricants and for water proofing.
14. Semiconductors conduct electricity better than insulators. They are also light sensitive.

SOLVED OBJECTIVE EXERCISE

Q1. Fill in the blanks.

(i) _____ acid has chemical formula HBO_2.
(ii) Aluminium normally occurs as _____ minerals found in the rock of outer portion of the earth ...
(iii) Aluminium gives _____ gas with hot concentrated H_2SO_4.
(iv) Boron forms _____ bond in its compounds.

(v) The chemical formula of white lead is _____.
(vi) _____ is the only element with less than four electrons in the outer most shell that is not metal.
(vii) In the Group IIIA of the periodic table, _____ is a semi-metal.
(viii) Borax that occurs as a natural deposit, is called _____.
(ix) Cryolite is an important mineral of aluminium and its formula is _____.
(x) A _____ is a substance that has different resistances to the passage of an electric current under different circumstances.

Answer Key.

(i)	Metaboric acid	(ii)	Alumino silicate
(iii)	(SO_2)	(iv)	3 covalent
(v)	$2PbCO_3.Pb(OH)_2$	(vi)	Boron
(vii)	Boron	(viii)	Tincal
(ix)	Na_3AlF_6	(x)	Semi conductor

Q2. Indicate True Or False.

(i) Boron always uses all the three of its valence electrons for bonding purposes.
(ii) Diaspore is an ore of carbon.
(iii) Emerald is an ore of aluminum that has the chemical formula $Al_2O_3.2SiO_2.2H_2O$.
(iv) An aqueous solution of borax is feebly acidic in nature
(v) In case of borax bead test, of Cupric oxide, the beads are coloured blue in the reducing flame.
(vi) Boric acid can be titrated with sodium hydroxide.
(vii) Carbon and silicon are the only non-metals in Group IVA.
(viii) PbO is commonly known as litharge.
(ix) Basic lead carbonate is a reddish brown pigment.
(x) Aluminium oxide (Al_2O_3) is also called bauxite.

Answer Key.

(i)	True	(ii)	False	(iii)	False	(iv)	False	(v)	False
(vi)	True	(vii)	True	(viii)	True	(ix)	False	(x)	False

Q3. Multiple Choice Questions. Encircle the correct answer.

(i) **Which metal is used in the thermit process because of its activity:**
(a) Iron (b) Copper (c) Aluminum (d) Zinc

(ii) **Aluminum oxide is:**
(a) Acidic oxide (b) Basic oxide (c) Amphoteric oxide (d) None of these

(iii) **Chemical compositions of colemanite is:**
(a) $Ca_2B_6O_{11}.5H_2O$ (b) $CaB_4O_7.4H_2O$ (c) $Na_2B_4O_7.4H_2O$ (d) $CaNaB_3O_9.8H_2O$

(iv) **Which element forms an ion with charge + 3:**
(a) Beryllium (b) Aluminium (c) Carbon (d) Silicon

(v) **Which electronic forms configuration corresponds to an element of Group – IIIA of the periodic, table**
(a) $1s^2, 2s^2, 2p^6, 3s^2, 3p^1$ (b) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, s^2$
(c) $1s^2, 2s^2, 2p^6$ (d) $1s^2, 2s^2, 2p^6, 3s^2, 3p^3$

(vi) **Which element among the following _____ belongs to Groups IVA of the periodic table:**
(a) Barium (b) Iodine (c) Lead (d) Oxygen

(vii) **Boric acid cannot be used:**
(a) as antiseptic in medicine (b) for washing eyes
(c) in soda bottles (d) for enamels and glazes

(viii) **Which of the following elements is not present abundantly in earth's crust?**
(a) Silicon (b) Aluminum (c) Sodium (d) Oxygen

(ix) **Tincal is a mineral of:**
(a) Al (b) B (c) Si (d) C

(x) **The chief ore of aluminium is:**
(a) Na_3AlF_6 (b) $Al_2O_3.2H_2O$ (c) Al_2O_3 (d) $Al_2O_3.H_2O$

Solved Exercise MCQ's

Q.No	Answer	Reason
(i)	(c) Aluminium	Aluminium has the tendency to react with both O_2 and N_2 so it reacts with air. The reaction is exothermic so used in thermite process.
(ii)	(c) Amphoteric oxide	Al_2O_3 reacts with acids as base and with bases as acid.
(iii)	(a) $Ca_2B_6O_{11}.5H_2O$	Colemanite is important mineral of B used to manufacture borax.
(iv)	(b) Aluminium	Aluminium loses 3 of its valence electrons to form Al^{+3} ion.
(v)	(a) $1s^2\ 2s^2\ sp^6\ 3s^2\ 3p^1$	Valence shell electronic configuration of Group-III A elements is ns^2np^1.
(vi)	(c) Lead	Group-IVA elements are C, Si, Ge, Sn and Pb.
(vii)	(c) In soda bottles	CO_2 is used in soda bottles and boric acid is not used.
(viii)	(c) Sodium	O, Si and Al are most abundant in earth's crust.
(ix)	(b) B	Tincal is natural deposit of borox.
(x)	(b) $Al_2O_3.2H_2O$	Bauxite ($Al_2O_3.2H_2O$) is the chief ore of aluminium

Previous Board Questions

1. What is Litharge? Give its chemistry.
2. Aqueous solution of borax is alkaline, why?
3. What are Semi-Conductors? Give its two uses.
4. What is the effect of temperature upon the viscosity of Silicones?
5. Write down four uses of Aluminium.
6. What is Borax bead test?
7. CO_2 in non-polar in nature. Give reason.
8. Explain why "CO_2 is acidic in nature."
9. Why is CO_2 a gas at room temperature while SiO_2 is solid?
10. Write names of these acids of Boron:
(i) H_3BO_3 (ii) HBO_2 (iii) $H_2B_4O_7$ (iv) $H_6B_4O_9$
11. How boric acid (H_3BO_3) reacts with ethyl alcohol and sodium carbonate?
12. Why are liquid silicones preferred over ordinary organic lubricants?
13. What happens when white lead is heated in air at about 340°C?
14. How entrapped bubbles of gases are removed from steel?
15. How will you prepare borax from
(a) Colemanite (b) Boric acid
16. Write down uses of boric acid.
17. Which basic radicals give the response to borax bead test?
18. What is the effect of temperature on semiconductors?
19. How borax reacts with HCl and H_2SO_4?
20. Give the reactions of aluminium with H_2SO_4 and NaOH

21. How weathering of potassium feldspar takes place? Explain with the help of a chemical equation.
22. Write chemical formulas of the following acids of boron.
(i) Orthoboric acid (ii) Metaboric acid (iii) Tetraboric acid
(iv) Pyroboric acid
23. What is meant by chemical garden? How can it be prepared.
24. What is the importance of oxides of lead in paints?
25. How aluminium reacts with
(a) Halogens (b) Acids
26. Why is aluminium not found as a free element?
27. What is the action of an aqueous solution of Borax on litmus?
28. Describe ring test.
29. Borax serves as water softening agent. Justify.

For Answers study
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CHAPTER 4

GROUP VA AND GROUP VIA ELEMENTS

GROUP VA ELEMENTS

Introduction

The elements of group VA of the periodic table comprise nitrogen, phosphorus, arsenic, antimony and bismuth.

Electronic Configurations and Physical Properties of Group VA Elements

Properties	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
Electronic configuration	$[He]2s^2 2p^3$	$[Ne]3s^2 3p^3$	$[Ar]3d^{10} 4s^2 4p^3$	$[Kr]4d^{10} 5s^2 5p^3$	$[Xe]5d^{10} 6s^2 6p^3$
Physical appearance	Colourless gas	Black Solid	Metallic solid	Metallic solid	Metallic solid
Ionization energy (kJ/mol)	1402	1012	950	830	700
Electron affinity (kJ/mol)	–7	–71.7	–77	–101	–110
Electronegativity	3.0	2.1	2.0	1.9	1.9
Atomic radius (pm)	70	110	121	141	157
Ionic radius of 3-ion (pm)	171	212	222	245	---
Melting points (°C)	–210	44	817	631	271
Boiling points (°C)	–196	280	613	1750	1560
Density (g/cm^3)	0.00125	1.83	5.73	6.68	9.80
Principal oxidation states	+3,+5	+3,+5	+3,+5	+3,+5	+3,+5

General Characteristics

(i) Metallic Character

- Nitrogen and phosphorus of group VA show the typical properties of non-metals. For example, they are poor conductors of heat and electricity and give acidic oxides. Their compounds are predominantly covalent.
- Arsenic and antimony are metalloids.
- However bismuth at the bottom of the group shows definite metallic properties.

The metallic character increases going down the group.

(ii) Bond Nature

Nitrogen has the greatest tendency to attract the electrons; antimony and bismuth have the least. The trend down the group also shifts from covalent bonding to ionic bonding.

(iii) Allotropes

Phosphorus, arsenic and antimony have allotropes. Allotropes of phosphorus i.e. red and white are more important.

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(iv) Common oxidation states

Phosphorus and other members of the group can make use of d orbitals in their bonding. This is because the energy of these orbitals is not much greater than those of the other valence shell orbitals. For example, phosphorus can make use of its 3s, 3p and the empty 3d orbitals during bonding with other elements.

In phosphorus one of the 3s electrons can be promoted to a vacant 3d orbital giving 5 unpaired electrons in the valence shell. Phosphorus can thus make three or five covalent bonds. Indeed three and five are the common valencies of the group VA elements.

Q. Why NCl_5 does not exist but PCl_5 does exist?

Nitrogen and its Compounds

Q4. (i) How does nitrogen differ from other elements of its group?

Ans.

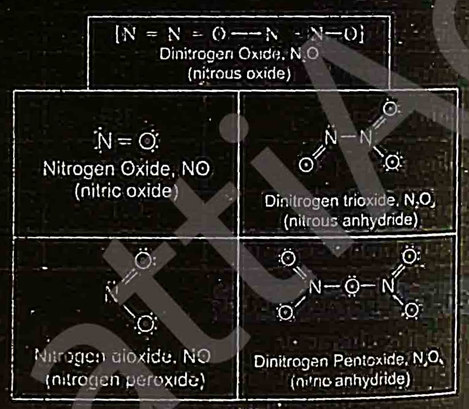
Nitrogen	Other Elements of V-A Group
(i) It is a gas	(i) Other elements of VA group are solids
(ii) It is diatomic molecule e.g. N_2	(ii) Other elements of V A group are tetra-atomic e.g. P_4, As_4, Sb_4.
(iii) It shows a large number of oxidation states from +5 to –3.	(iii) Other elements show limited number of oxidation states which is +5 & +3.
(iv) It occurs in free state as well as in combined states.	(iv) The other elements of group V-A occur in combined states only.
(v) It does not form complexes due to non-availability of "d" orbitals.	(v) Other elements which have empty "d" orbitals can accept electron pairs to form complexes.
(vi) It is a typical non-metal.	(vi) As and Sb are metalloids and Bi is a metal.

Occurrence

- Nitrogen is present **in free state** in air as a major constituent 78% by volume. It is an inactive gas in comparison with oxygen which is the next major constituent of air.
- Inorganic compounds of nitrogen are not commonly found as minerals.
- **In combined state** nitrogen is found in all living matter including animals and plants in the form of proteins, urea and amino acids.

Oxides of Nitrogen

Nitrogen forms several oxides with oxygen. Common oxides of nitrogen are N_2O, NO and NO_2. It also forms N_2O_3 and N_2O_5.



Oxides of Nitrogen

1. Dinitrogen Oxide (N_2O or Nitrous oxide)

Preparation

1. Dinitrogen oxide can be prepared by the action of dil. HNO_3 on metallic zinc.

$$4Zn_{(s)} + 10HNO_{3(dil.)} \longrightarrow 4Zn(NO_3)_{2(aq)} + N_2O_{(g)} + 5H_2O_{(l)}$$

2. It is usually prepared by heating ammonium nitrate to about 200°C

$$NH_4NO_{3(s)} \longrightarrow N_2O_{(g)} + 2H_2O_{(l)}$$

To avoid the danger of explosion, ammonium nitrate can be replaced by a mixture of sodium nitrate and ammonium sulphate.

Properties

- Dinitrogen oxide is a colourless gas with a faint, pleasant smell and a sweetish taste.
- It is fairly soluble in cold water.
- **Laughing gas:** A mixture of N_2O with a little oxygen, if inhaled for a sufficiently long time, produces hysterical laughter, hence it is also known as "laughing gas". It is used in dental surgery.

Pure N_2O is fatal and dangerous. N_2O with 10% O_2 acts as mild anaesthetic agent.

Reactions

1. It is not combustible but resembles oxygen in rekindling a glowing splinter. Similarly, it supports combustion if burning substances, such as sulphur, phosphorus, etc. are taken in the cylinder containing this gas.

$$S_{(s)} + 2N_2O_{(g)} \longrightarrow SO_{2(g)} + 2N_{2(g)}$$

$$P_{4(s)} + 10N_2O_{(g)} \longrightarrow P_4O_{10(s)} + 10N_{2(g)}$$

2. When N_2O is passed over red hot copper, it is reduced to nitrogen.

$$Cu_{(s)} + N_2O_{(g)} \longrightarrow CuO_{(s)} + N_{2(g)}$$

2. Nitrogen Oxide (NO or Nitric oxide)

Preparation

1. Nitrogen oxide can be prepared by the action of dil. HNO_3 on copper.

$$3Cu_{(s)} + 8HNO_{3(dil.)} \longrightarrow 3Cu(NO_3)_{2(aq)} + 2NO_{(g)} + 4H_2O_{(l)}$$

2. It can also be prepared by passing air through an electric arc.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

Properties

Nitrogen oxide is a colourless gas heavier than air and sparingly soluble in water.

Reactions

1. With oxygen, it forms reddish brown nitrogen dioxide.

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

2. It decomposes into N_2 and O_2 at about 1000°C and supports combustion.

$$2NO_{(g)} \longrightarrow N_{2(g)} + O_{2(g)}$$

3. It forms nitrosyl chloride and nitrosyl bromide with chlorine and bromine, respectively in the presence of charcoal.

$$2NO_{(g)} + Cl_{2(g)} \longrightarrow 2NOCl_{(g)}$$

Q.10 (i) Describe "Ring test" for the confirmation of the presence of nitrate ions in solution.

Ans

Ring Test

This is a confirmatory test for nitrate NO_3^{-1} ion. The respected nitrate is dissolved in water and some fresh $FeSO_4$ solution is added to it. Concentrated sulphuric acid is slowly run down the side of the test tube. Brown ring is formed at the junction of two solutions which confirms the presence of nitrate ion.

$$FeSO_{4(aq)} + NO_{(g)} \longrightarrow FeSO_4.NO_{(aq)}$$

$$NO_3^{-1} + 3Fe^{+2} + 4H^{+1} \longrightarrow NO + 3Fe^{+3} + 2H_2O$$

$$Fe^{+2} + NO + 5H_2O \longrightarrow [Fe(H_2O)_5NO]$$

Brown ring

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With reducing agents, it is reduced to nitrous oxide or nitrogen.

$$H_2S_{(g)} + 2NO_{(g)} \longrightarrow H_2O_{(g)} + N_2O_{(g)} + S_{(s)}$$

$$H_2SO_{3(aq)} + 2NO_{(g)} \longrightarrow H_2SO_{4(aq)} + N_2O_{(g)}$$

Q. How does nitrogen oxide (NO) act as reducing and oxidizing agent?

5. Oxidizing agents can oxide NO to NO_2 or HNO_3

$$2HNO_{3(aq)} + NO_{(g)} \longrightarrow H_2O_{(\ell)} + 3NO_{2(g)}$$

$$6KMnO_{4(aq)} + 12H_2SO_{4(aq)} + 10NO_{(g)} \longrightarrow 6KHSO_{4(aq)} + 6MnSO_{4(aq)} + 10HNO_{3(aq)} + 4H_2O_{(\ell)}$$

3. Nitrogen Dioxide (NO_2)

Preparation

1. It can be prepared in small quantities by heating lead nitrate.

$$2Pb(NO_3)_{2(s)} \longrightarrow 2PbO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

Q.8 Describe the preparation of NO_2 gas. Also give its reactions.

2. It can also be prepared by reacting conc. HNO_3 with copper.

$$Cu_{(s)} + 4HNO_3\,(conc.) \longrightarrow Cu(NO_3)_{2(aq)} + 2H_2O_{(\ell)} + 2NO_{2(g)}$$

Properties of Nitrogen Dioxide

- Nitrogen dioxide is a reddish brown gas with a pungent smell.
- It dissolves readily in water to form a blue acidic solution.

Q. What is the effect of temperature on NO_2?

Reactions

1. Heating effect

On cooling, NO_2 is converted into a yellow liquid which can be frozen to a colourless solid dinitrogen tetraoxide (N_2O_4). If this solid is heated to 140°C, the mixture contains NO_2 and N_2O_4 but above 140°C NO_2 is converted to NO and O_2 molecules which are colourless. This decomposition is complete at 620°C.

$$NO_{2(g)} \rightarrow NO_{2(\ell)} \rightarrow N_2O_{4(\ell)} \underset{}{\overset{140°C}{\rightleftharpoons}} 2NO_{2(g)} \overset{620°C}{\rightleftharpoons} 2NO_{(g)} + O_{2(g)}$$

Pale Yellow — Reddish brown — Colourless

2. Decomposition

Elements like phosphorus, potassium and carbon continue burning in NO_2 as it yields O_2 on decomposition.

$$2NO_{2(g)} \longrightarrow 2NO_{(g)} + O_{2(g)}$$

$$2P_{(s)} + 5NO_{2(g)} \longrightarrow P_2O_{5(s)} + 5NO_{(g)}$$

3. Dissolution in water

In the absence of air, it dissolves in water to form nitric and nitrous acids.

$$2NO_{2(g)} + H_2O_{(\ell)} \longrightarrow HNO_{3(aq)} + HNO_{2(aq)}$$

However in the presence of air or oxygen, nitric acid is the final product.

$$4NO_{2(g)} + 2H_2O_{(\ell)} + O_{2(g)} \longrightarrow 4HNO_{3(aq)}$$

4. Reaction with alkalies

A mixture of nitrate and nitrite is formed when NO_2 is passed through strong alkalies.

$$2NaOH_{(aq)} + 2NO_{2(g)} \longrightarrow NaNO_{3(aq)} + NaNO_{2(aq)} + H_2O_{(\ell)}$$

$$2KOH_{(aq)} + 2NO_{2(g)} \longrightarrow KNO_{3(aq)} + KNO_{2(aq)} + H_2O_{(\ell)}$$

Q.10 (ii) NO_2 is a strong oxidizing agent. Prove the truth of this statement giving examples.

Ans **NO_2 – As an oxidizing agent:**

It is a strong oxidizing agent and oxidizes H_2S to sulphur, ferrous sulphates to ferric sulphates and KI to I_2.

$$H_2S_{(g)} + NO_{2(g)} \longrightarrow H_2O_{(\ell)} + S_{(s)} + NO_{(g)}$$

$$2FeSO_{4(aq)} + H_2SO_{4(aq)} + NO_{2(g)} \longrightarrow Fe_2(SO_4)_{3(aq)} + H_2O_{(\ell)} + NO_{(g)}$$

$$2KI_{(aq)} + 2NO_{2(g)} \longrightarrow 2KNO_{2(aq)} + I_{2(s)}$$

Oxyacids of Nitrogen

There are two important oxyacids of nitrogen, nitrous acid and nitric acid.



Nitrous acid, HNO_2 | Nitric acid, HNO_3

Hyponitrous Acid (HNO)	Reducing agent
Nitrous Acid (HNO_2)	Reducing agent & Oxidizing agent
Nitric Acid (HNO_3)	Oxidizing agent

Nitrous Acid (HNO_2)

Preparation

1. It can be prepared by dissolving dinitrogen trioxide in water at 0°C

$$N_2O_{3(g)} + H_2O_{(\ell)} \longrightarrow 2HNO_{2(aq)}$$

2. Pure nitrous acid solution can be prepared by reaction between ice cold barium nitrite solution and ice cold dilute sulphuric acid.

$$Ba(NO_2)_{2(aq)} + H_2SO_{4(aq)} \longrightarrow BaSO_{4(aq)} + 2HNO_{2(aq)}$$

Properties

It is only known in the form of its salts and is stable to some extent in a dilute solution.

Reactions

Decomposition

It begins to decompose almost as soon as it is formed even at ordinary temperature.

$$3HNO_{2(aq)} \longrightarrow HNO_{3(aq)} + 2NO_{(g)} + H_2O_{(g)}$$

Q. HNO_2 is oxidizing agent as well as reducing agent. Explain by giving examples.

Ans **(i) HNO_2 – As an oxidizing agent**

It acts as an oxidizing agent and oxidizes HI, SO_2 and $SnCl_2$ into I_2, H_2SO_4 and $SnCl_4$, respectively.

$$2HNO_{2(aq)} + 2HI_{(aq)} \longrightarrow 2H_2O_{(\ell)} + 2NO_{(g)} + I_{2(s)}$$

$$2HNO_2 \longrightarrow H_2O + 2NO + [O]$$

$$SO_{2(g)} + H_2O_{(\ell)} + [O]_{(g)} \longrightarrow H_2SO_{4(aq)}$$

$$SnCl_{2(aq)} + 2HCl_{(aq)} + 2HNO_{2(aq)} \longrightarrow SnCl_{4(aq)} + 2NO_{(g)} + 2H_2O_{(\ell)}$$

(ii) HNO_2 – As a reducing agent

Nitrous acid decolorizes acidified $KMnO_4$ and bromine water. It readily gets oxidized to nitric acid, so it also behaves as a reducing agent.

$$2KMnO_{4(aq)} + 3H_2SO_{4(aq)} + 5HNO_{2(aq)} \longrightarrow K_2SO_{4(aq)} + 2MnSO_{4(aq)} + 3H_2O_{(\ell)} + 5HNO_{3(aq)}$$

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$$HNO_{2(aq)} + Br_{2(aq)} + H_2O_{(\ell)} \longrightarrow HNO_{3(aq)} + 2HBr_{(aq)}$$

Reaction with alkalies

As an acid it reacts with alkalies producing salts.

$$NaOH_{(aq)} + HNO_{2(aq)} \longrightarrow NaNO_{2(aq)} + H_2O_{(\ell)}$$

Reaction with organic compounds containing NH_2 group

It also reacts with organic compounds containing NH_2 group and produces nitrogen.

$$2HNO_{2(aq)} + CO(NH_2)_{2(aq)} \longrightarrow 2N_{2(g)} + CO_{2(g)} + 3H_2O_{(\ell)}$$

Urea

$$HNO_{2(aq)} + C_6H_5NH_{2(\ell)} \longrightarrow C_6H_5OH_{(\ell)} + N_{2(g)} + H_2O_{(\ell)}$$

Aminobenzene Phenol

MCQ's

The gas evolved when nitrous acid reacts with organic compounds containing NH_2 group?

(a) N_2 (b) H_2
(c) NH_3 (d) NO_2

NITRIC ACID (HNO_3)

Laboratory Preparation

In the laboratory, nitric acid is prepared by heating potassium nitrate crystals with concentrated sulphuric acid.

$$KNO_{3(s)} + H_2SO_{4(conc.)} \longrightarrow KHSO_{4(aq)} + HNO_{3(aq)}$$

Commercial preparation of Nitric Acid

Q.5 (a) Explain the Birkeland and Eyde's process for the manufacture of nitric acid?

Ans: Birkeland and Eyde's process

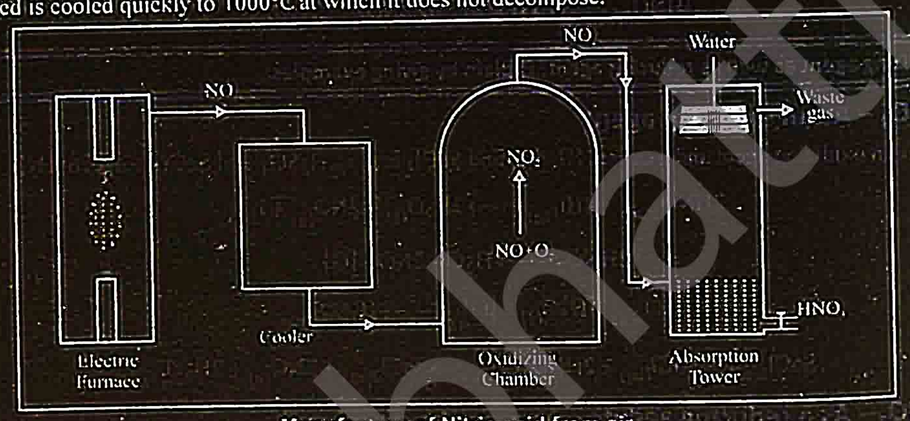
This process consists of the following steps:

(i) Formation of nitric oxide

Atmospheric nitrogen and oxygen are combined to give nitric oxide in an electric arc (3000°C).

$$N_{2(g)} + O_{2(g)} \xrightarrow{3000°C} 2NO_{(g)}$$

NO formed is cooled quickly to 1000°C at which it does not decompose.



Manufacture of Nitric acid from air

(ii) Oxidation of nitric oxide

At 600°C, NO combines with O_2 to form NO_2

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

(iii) Dissolution in water

Nitrogen dioxide is absorbed in water to give dilute HNO_3 along with nitrous acid.

$$2NO_{2(g)} + H_2O_{(\ell)} \longrightarrow HNO_{3(aq)} + HNO_{2(aq)}$$

(iv) Oxidation of nitrous acid

Nitrous acid is oxidized to nitric acid and nitric oxide which is re-oxidized to NO_2.

$$3HNO_{2(aq)} \longrightarrow HNO_{3(aq)} + 2NO_{(g)} + H_2O_{(\ell)}$$

Properties of Nitric Acid

- Concentrated nitric acid is a colourless volatile liquid which fumes strongly in air.
- It has a pungent smell.
- Its specific gravity at 15°C is 1.53.

Q5. (c) What is meant by fuming nitric acid?

Ans **Fuming Nitric acid:**

A mixture of conc. HNO_3 and NO_2 is called fuming nitric acid. It is more reactive than conc. HNO_3. It is a red or pale yellow fuming liquid.

Reactions

1. Decomposition

Nitric acid is decomposed in the presence of light even at ordinary temperature.

$$4HNO_{3(aq)} \longrightarrow 2H_2O_{(\ell)} + 4NO_{2(g)} + O_{2(g)}$$

2. HNO_3 – As an acid

It is a very strong acid. It exhibits all the usual general properties of acids in all reactions where its oxidizing properties are not shown. It reacts in normal way with basic oxides, hydroxides and carbonates forming respective salts.

$$2HNO_{3(aq)} + CaO_{(aq)} \longrightarrow H_2O_{(\ell)} + Ca(NO_3)_{2(aq)}$$

$$HNO_{3(aq)} + NaOH_{(aq)} \longrightarrow H_2O_{(\ell)} + NaNO_{3(aq)}$$

$$2HNO_{3(aq)} + Na_2CO_{3(aq)} \longrightarrow 2NaNO_{3(aq)} + H_2O_{(\ell)} + CO_{2(aq)}$$

3. HNO_3 – As an oxidizing agent

It acts as a strong oxidizing agent due to the ease with which it is decomposed.

$$2HNO_{3(aq)} \longrightarrow H_2O_{(\ell)} + 2NO_{2(g)} + [O]_{(g)}$$

(i) With Non-metals

It oxidizes non-metals to their corresponding oxides.

$$C_{(s)} + 4HNO_{3(aq)} \longrightarrow CO_{2(g)} + 4NO_{2(g)} + 2H_2O_{(\ell)}$$

$$S_{(s)} + 6HNO_{3(aq)} \longrightarrow 2H_2O_{(\ell)} + 6NO_{2(g)} + H_2SO_{4(aq)}$$

$$5HNO_{3(aq)} + P_{(s)} \longrightarrow H_3PO_{4(aq)} + H_2O_{(\ell)} + 5NO_{2(g)}$$

Q.10(iii) Write down the chemical equations and names of the products formed as a result of the reaction of HNO_3 with arsenic and antimony.

Ans **(ii) With Metalloids**

Arsenic and antimony are metalloids they can be oxidized to their corresponding acids when react with Conc. Nitric acid.

$$As_{(s)} + 5HNO_{3(aq)} \longrightarrow \underset{\text{(Arsenic Acid)}}{H_3AsO_{4(aq)}} + 5NO_{2(g)} + H_2O_{(\ell)}$$

Arsenic

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$$Sb_{(g)} + 5HNO_{3(aq)} \longrightarrow \underset{\text{(Stibnic Acid)}}{H_3SbO_{4(aq)}} + 5NO_{2(g)} + H_2O_{(\ell)}$$
Antimony

(iii) With Metals

Nitric acid behaves differently with different metals.

(a) Gold, platinum, iridium and titanium do not react.

(b) Iron, cobalt, nickel, chromium, aluminium are rendered passive by acid due to the formation of a film of their oxides over them.

(c) Tungsten (W) and uranium (U) are changed into their oxides.

(d) Magnesium, calcium and manganese give hydrogen with dilute nitric acid.

$$Mg_{(s)} + 2HNO_{3(dil.)} \longrightarrow Mg(NO_3)_{2(aq)} + H_{2(g)}$$

$$Mn_{(s)} + 2HNO_{3(dil.)} \longrightarrow Mn(NO_3)_{2(aq)} + H_{2(g)}$$

Q5. (b) Which metals evolve hydrogen upon reaction with nitric acid? Illustrate along with chemical equations.

(e) Copper and lead give nitric oxide with dilute acid and nitrogen dioxide with concentrated acid.

$$3Cu_{(s)} + 8HNO_{3(dil.)} \longrightarrow 3Cu(NO_3)_{2(aq)} + 2NO_{(g)} + 4H_2O_{(\ell)}$$

$$Cu_{(s)} + 4HNO_{3(conc.)} \longrightarrow Cu(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O_{(\ell)}$$

(f) Mercury gives mercurous nitrate and nitric oxide with dilute nitric acid.

$$6Hg_{(\ell)} + 8HNO_{3(dil.)} \longrightarrow 3Hg_2(NO_3)_{2(aq)} + 2NO_{(g)} + 4H_2O_{(\ell)}$$

With concentrated acid, it gives mercuric nitrate and NO_2.

$$Hg_{(\ell)} + 4HNO_{3(conc)} \longrightarrow Hg(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O_{(\ell)}$$

(g) Silver reacts with nitric acid to give silver nitrate and nitric oxide.

$$3Ag_{(s)} + 4HNO_{3(aq)} \longrightarrow 3AgNO_{3(aq)} + NO_{(g)} + 2H_2O_{(\ell)}$$

(h) Dilute nitric acid gives ammonium nitrate, when it reacts with tin. With concentrated acid meta-stannic acid is produced.

$$4Sn_{(s)} + 10HNO_{3(dil.)} \longrightarrow 4Sn(NO_3)_2 + NH_4NO_{3(aq)} + 3H_2O_{(\ell)}$$

$$Sn_{(s)} + 4HNO_{3(conc.)} \longrightarrow H_2SnO_{3(aq)} + 4NO_{2(g)} + H_2O_{(\ell)}$$

(i) Zinc gives different products depending upon the concentration of acid and temperature. Very dilute nitric acid gives NH_4NO_3. Moderately dilute nitric acid gives nitrous oxide while concentrated nitric acid gives NO_2.

$$4Zn_{(s)} + 10HNO_{3(v.dil.)} \longrightarrow 4Zn(NO_3)_{2(aq)} + NH_4NO_{3(aq)} + 3H_2O_{(\ell)}$$

$$4Zn_{(s)} + 10HNO_{3(dil.)} \longrightarrow 4Zn(NO_3)_{2(aq)} + N_2O_{(g)} + 5H_2O_{(\ell)}$$

$$Zn_{(s)} + 4HNO_{3(conc.)} \longrightarrow Zn(NO_3)_{2(s)} + 2NO_2 + 2H_2O_{(\ell)}$$

4. With Reducing agents

Reducing agents like $FeSO_4$, H_2S and HI are converted to $Fe_2(SO_4)_3$, S and I_2 respectively, when they react with conc. HNO_3.

$$6FeSO_{4(aq)} + 3H_2SO_{4(aq)} + 2HNO_{3(conc.)} \longrightarrow 3Fe_2(SO_4)_{3(aq)} + 2NO_{(g)} + 4H_2O_{(\ell)}$$

$$2HNO_{3(conc.)} + 3H_2S_{(g)} \longrightarrow 4H_2O_{(\ell)} + 2NO_{(g)} + 3S_{(s)}$$

$$6HI_{(aq)} + 2HNO_{3(conc.)} \longrightarrow 4H_2O_{(\ell)} + 2NO_{(g)} + 3I_{2(s)}$$

Q.4 (ii) Why does aqua regia dissolve gold and platinum?

Ans: Aqua Regia

When one volume of concentrated HNO_3 is mixed with 3 volumes of concentrated HCl, aqua regia is formed. It is employed to dissolve gold and platinum.

$$HNO_{3(conc.)} + 3HCl_{(conc.)} \longrightarrow NOCl_{(aq)} + 2H_2O_{(\ell)} + Cl_{2(g)}$$

NOCl formed is decomposed giving NO and nascent chlorine[Cl].

$$NOCl \longrightarrow NO_{(g)} + [Cl]_{(g)}$$

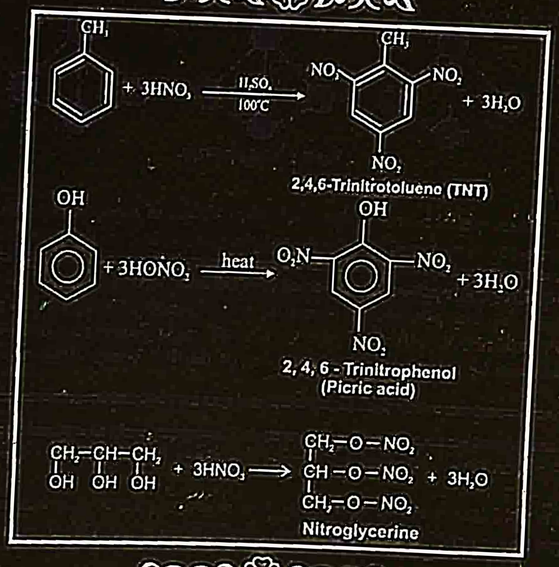
The nascent chlorine[Cl] thus formed converts the noble metals such as gold and platinum into their water soluble chlorides.

$$Au_{(s)} + 3[Cl]_{(aq)} \longrightarrow AuCl_{3(aq)}$$
$$Pt_{(s)} + 4[Cl]_{(aq)} \longrightarrow PtCl_{4(aq)}$$

Uses of Nitric acid

It is used:

1. as a laboratory reagent.
2. in the manufacture of nitrogenous fertilizers.
3. in the manufacture of explosives.
4. for making organic dyes and varnishes.



Phosphorus and its compounds

Occurrence

- Phosphorus is the second member of group VA. Its name comes from Greek word meaning "Light bearing".

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- Unlike nitrogen, it does not occur in free state in nature. Most of the phosphorus is found in deposits of phosphate rocks, i.e. impure $Ca_3(PO_4)_2$ and apatite $Ca_5F(PO_4)_3$.
- As a constituent of plant and animal tissues, it is essential for their normal growth. It occurs especially in seeds, the yolk of eggs, the nerves, brain and bone marrows, usually in the form of lecithins.
- In the form of calcium phosphate, it is essential constituent of bone. Bone ash which contains 80% calcium phosphate $Ca_3(PO_4)_2$ is an important source of phosphorus.

Allotropes of phosphorus

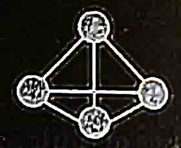
Phosphorus can exist in at least six different solid allotropic forms which are

(i) White/Yellow phosphorus (ii) Red phosphorus (iii) α -black phosphorus
(iv) β-black phosphorus (v) Violet phosphorus (vi) Scarlet phosphorus

We will mention only three here:

1. White phosphorus

- **Physical properties:** White phosphorus is a very reactive, poisonous, volatile, waxy, yellowish white substance which is soluble in benzene and carbon disulphide.
- **Structure:** It exists in the form of tetra atomic molecules (P_4) which have a tetrahedral structure.

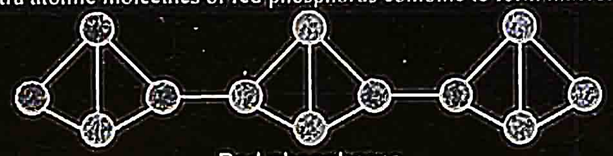


White phosphorus

- **Heating effect:** It boils at 280°C to P_4 vapours which dissociate above 700°C to form P_2 molecules.

2. Red phosphorus

- **Physical properties:** Red phosphorus is less reactive and less poisonous than white phosphorus.
- **Preparation:** It is prepared by heating white phosphorus in the presence of little iodine or sulphur as a catalyst upto 250°C in vacuum. The tetra atomic molecules of red phosphorus combine to form macromolecules.



Red phosphorus

3. Black phosphorus

- **Physical properties:** Black phosphorus is the third form which is most stable and least reactive under ordinary conditions. Black phosphorus is prepared by heating red phosphorus to high temperature and pressure.

Q. White phosphorus is a very reactive allotrope of phosphorus. Justify?

Ans. In white phosphorus, the four phosphorus atoms lie at the corners of a regular tetrahedron. The P-P-P bond angle in a tetrahedral P_4 molecule is only 60°. This very small angle produces a considerable amount of strain in the P_4 molecule, which can be relieved by breaking one of the P-P bonds. Thus white phosphorus is very reactive allotrope.

- White phosphorus when comes in contact with air, it undergoes slow combustion and glows in dark. It is called **phosphorescence.**
- White phosphorus is toxic and when contacts with skin, produces painful slow heating burns.
- In phosphorus, bond angle is 60° which is less than normal bond angle. Due to smaller angle, it has strain and very **reactive.**
- White phosphorus consists of individual tetrahedral P_4 molecules. It is a waxy solid that melts at 44°C and boils at 280°C.
- Red phosphorus is used to make incendiary devices (bombs, fireworks etc). Red phosphorus when mixed with sand is used as the rubbing surface of the match box.
- Black phosphorus has flaky appearance due to layers.

Halides of Phosphorus

Phosphorus Trichloride (PCl_3)

Preparation

1. It is usually prepared by melting white phosphorus in a retort in an inert atmosphere of CO_2 and current of dried chlorine is passed over it. The vapours of PCl_3 are collected in a flask kept in ice-bath.

$$2P_{(s)} + 3Cl_{2(g)} \longrightarrow 2PCl_{3(\ell)}$$

2. It may also be prepared by the action of phosphorus with thionyl chloride.

$$2P_{(s)} + 4SOCl_{2(\ell)} \longrightarrow 2PCl_{3(\ell)} + 2SO_{2(g)} + S_2Cl_{2(s)}$$

Properties of PCl_3

It is a colourless fuming liquid which boils at 76°C and freezes at -112°C.

Chemical Reactions

1. It combines with chlorine to form phosphorus pentachloride.

$$PCl_{3(\ell)} + Cl_{2(g)} \longrightarrow PCl_{5(s)}$$

2. It combines with atmospheric oxygen slowly to form phosphorus oxychloride.

$$2PCl_{3(\ell)} + O_{2(g)} \longrightarrow 2POCl_{3(s)}$$

3. It is soluble in organic solvents, but readily reacts with water to form phosphorus acid.

$$PCl_{3(\ell)} + 3H_2O_{(\ell)} \longrightarrow H_3PO_{3(aq)} + 3HCl_{(aq)}$$

4. It reacts with alcohols and carboxylic acids forming the respective chloro derivatives and H_3PO_3.

$$3CH_3OH_{(\ell)} + PCl_{3(\ell)} \longrightarrow 3CH_3Cl_{(\ell)} + H_3PO_{3(\ell)}$$

$$3CH_3COOH_{(\ell)} + PCl_{3(\ell)} \longrightarrow 3CH_3COCl_{(\ell)} + H_3PO_{3(\ell)}$$

Phosphorus Pentachloride (PCl_5)

Preparation

1. By passing dry chlorine through phosphorus trichloride at temperature of about 0°C, phosphorus pentachloride is formed.

$$PCl_{3(\ell)} + Cl_{2(g)} \longrightarrow PCl_{5(s)}$$

2. It may also be prepared by passing dry chlorine in a well cooled solution of phosphorus in carbon disulphide.

$$2P_{(\ell)} + 5Cl_{2(g)} \longrightarrow 2PCl_{5(s)}$$

Properties of PCl_5

It is yellowish white crystalline solid which sublimes at about 100°C. It gives fumes in moist air with an irritating smell.

Chemical Reactions

1. It decomposes on heating producing PCl_3 and chlorine.

$$PCl_{5(s)} \longrightarrow PCl_{3(\ell)} + Cl_{2(g)}$$

2. It gets decomposed by water forming phosphorus oxychloride which further reacts with water to produce phosphoric acid.

$$PCl_{5(s)} + H_2O_{(\ell)} \longrightarrow POCl_{3(\ell)} + 2HCl_{(aq)}$$

$$POCl_{3(\ell)} + 3H_2O_{(\ell)} \longrightarrow H_3PO_{4(aq)} + 3HCl_{(aq)}$$

$$PCl_{5(s)} + 4H_2O_{(\ell)} \longrightarrow H_3PO_{4(aq)} + 5HCl_{(aq)}$$

3. It converts metals into their chlorides.

$$Zn_{(s)} + PCl_{5(s)} \longrightarrow ZnCl_{2(s)} + PCl_{3(\ell)}$$

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Halide of phosphorus	Hybridization	Structure	Physical State
PCl_3	sp^3	Trigonal pyramidal	Colourless fuming liquid
PCl_5	dsp^3	Trigonal bipyramidal	Yellowish white crystalline solid

Oxides of Phosphorus

Phosphorus Trioxide $P_2O_3(P_4O_6)$

Preparation

P_2O_3 can be prepared by burning white phosphorus in a limited supply of air.

$$P_{4(s)} + 3O_{2(g)} \longrightarrow 2P_2O_{3(s)}$$

Properties of P_2O_3

- It is a white waxy solid with garlic like odour.
- It melts at 22.8°C and boils at 173°C.
- It is highly poisonous in nature.

Chemical reactions

1. When heated in the presence of air (oxygen), it is converted into phosphorus pentoxide.

$$P_2O_{3(s)} + O_{2(g)} \longrightarrow P_2O_{5(s)}$$

2. It reacts with cold water to give phosphorus acid.

$$P_2O_{3(s)} + 3H_2O_{(\ell)} \longrightarrow 2H_3PO_{3(s)}$$

Q. How does P_2O_3 react with cold & hot water?

With hot water, it forms phosphine and phosphoric acid.

$$2P_2O_{3(s)} + 6H_2O_{(\ell)} \longrightarrow 3H_3PO_{4(aq)} + PH_{3(g)}$$

Phosphorus Pentoxide $P_2O_5(P_4O_{10})$

Preparation:

It is prepared by burning phosphorus in excess of dry air.

$$P_{4(s)} + 5O_{2(g)} \longrightarrow 2P_2O_{5(s)}$$

Properties of P_2O_5

- It is a white hygroscopic powder having a faint, garlic like odour due to the presence of traces of P_2O_3.
- It sublimes at 360°C.

Chemical Reactions

Q. How does P_2O_5 react with cold & hot water?

1. With cold water, phosphorus pentoxide forms metaphosphoric acid.

$$P_2O_{5(s)} + H_2O_{(\ell)} \longrightarrow 2HPO_{3(aq)}$$

With hot water, it forms orthophosphoric acid.

$$P_2O_{5(s)} + 3H_2O_{(\ell)} \longrightarrow 2H_3PO_{4(aq)}$$

Q.10 (v) P_2O_5 is a powerful dehydrating agent. Prove giving examples.

Ans. It is a powerful dehydrating agent, thus, with HNO_3, H_2SO_4, CH_3COOH and C_2H_5OH, it gives N_2O_5, SO_3, $(CH_3CO)_2O$ and C_2H_4 respectively.

$$2HNO_{3(aq)} + P_2O_{5(s)} \longrightarrow N_2O_{5(g)} + 2HPO_{3(aq)}$$

$$H_2SO_{4(aq)} + P_2O_{5(s)} \longrightarrow SO_{3(g)} + 2HPO_{3(aq)}$$

$$2CH_3COOH_{(aq)} + P_2O_{5(s)} \longrightarrow (CH_3CO)_2O_{(\ell)} + 2HPO_{3(aq)}$$

Acetic anhydride

$$C_2H_5OH_{(\ell)} + P_2O_{5(s)} \longrightarrow C_2H_{4(g)} + 2HPO_{3(aq)}$$

Ethene

Oxyacids of phosphorus

Oxoacids of phosphorus

Hypophosphorus acid	H_3PO_2
Phosphorus acid	H_3PO_3
Hypophosphoric acid	$H_4P_2O_6$
Orthophosphoric acid	H_3PO_4
Pyrophosphoric acid	$H_4P_2O_7$
Metaphosphoric acid	HPO_3
Peroxophosphoric acid	H_3PO_5

Phosphorus acid (H_3PO_3)

Preparation

1. It is prepared by dissolving phosphorus trioxide in cold water.

$$P_2O_{3(s)} + 3H_2O_{(\ell)} \longrightarrow 2H_3PO_{3(aq)}$$

2. It is also obtained by the hydrolysis of phosphorus trichloride.

$$PCl_{3(\ell)} + 3H_2O_{(\ell)} \longrightarrow H_3PO_{3(aq)} + 3HCl_{(aq)}$$

Properties of H_3PO_3

It is a white crystalline solid, which melts at 73.6°C.

Chemical Reactions

Q. How phosphorus acid acts as reducing agent?

1. It decomposes into phosphine and orthophosphoric acid on heating.

$$4H_3PO_{3(s)} \longrightarrow 3H_3PO_{4(s)} + PH_{3(g)}$$

2. It is a powerful reducing agent and reduces $CuSO_4$, $AgNO_3$, etc. to the metallic state.

$$H_3PO_{3(s)} + CuSO_{4(aq)} + H_2O_{(\ell)} \longrightarrow H_3PO_{4(aq)} + H_2SO_{4(aq)} + Cu_{(s)}$$

$$H_3PO_{3(s)} + 2AgNO_{3(aq)} + 2NH_4OH_{(aq)} \longrightarrow H_3PO_{4(aq)} + 2NH_4NO_{3(aq)} + H_2O_{(\ell)} + 2Ag_{(s)}$$

3. It reacts with oxygen to form orthophosphoric acid.

$$2H_3PO_{3(s)} + O_{2(g)} \longrightarrow 2H_3PO_{4(s)}$$

4. Nascent hydrogen produced by Zn/HCl reduces H_3PO_3 to phosphine.

$$H_3PO_{3(s)} + 6[H]_{(g)} \longrightarrow PH_{3(g)} + 3H_2O_{(\ell)}$$

Orthophosphoric acid (H_3PO_4)

Preparation

1. It is prepared by dissolving phosphorus pentoxide in hot water.

$$P_2O_{5(s)} + 3H_2O_{(\ell)} \longrightarrow 2H_3PO_{4(aq)}$$

2. It is also obtained by heating red phosphorus with concentrated HNO_3.

$$P_{(s)} + 5HNO_{3(conc.)} \longrightarrow H_3PO_{4(aq)} + 5NO_{2(g)} + H_2O_{(\ell)}$$

3. Hydrolysis of phosphorus pentachloride also gives orthophosphoric acid.

$$PCl_{5(\ell)} + 4H_2O_{(\ell)} \longrightarrow H_3PO_{4(aq)} + 5HCl(aq)$$

4. On large scale, it can be prepared by heating a mixture of phosphorite (bone ash) and sand in an electric furnace. The phosphorus pentoxide formed is treated with hot water to obtain phosphoric acid.

$$Ca_3(PO_4)_{2(s)} + 3SiO_{2(s)} \longrightarrow 3CaSiO_{3(s)} + P_2O_{5(s)}$$

$$P_2O_{5(s)} + 3H_2O_{(\ell)} \longrightarrow 2H_3PO_{4(aq)}$$

Properties of H_3PO_4

- It is a colourless, deliquescent crystalline solid.

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- It melts at 41°C.
- It is soluble in water.

Chemical Reactions

1. It is a weak tribasic acid. It reacts with NaOH to give three series of salts.

(i) $H_3PO_{4(aq)} + NaOH_{(aq)} \longrightarrow NaH_2PO_{4(aq)} + H_2O_{(\ell)}$

(ii) $NaH_2PO_{4(aq)} + NaOH_{(aq)} \longrightarrow Na_2HPO_{4(aq)} + H_2O_{(\ell)}$

(iii) $Na_2HPO_{4(aq)} + NaOH_{(aq)} \longrightarrow Na_3PO_{4(aq)} + H_2O_{(\ell)}$

2. On heating, it loses water and converted into pyro and metaphosphoric acid.

$$\underset{\text{Orthophosphoric acid}}{2H_3PO_4} \xrightarrow[-H_2O]{240^\circ C} \underset{\text{Pyrophosphoric acid}}{H_4P_2O_7} \xrightarrow[-H_2O]{316^\circ C} \underset{\text{Metaphosphoric acid}}{2HPO_3}$$

Q. Compare the properties of P_2O_3 and P_2O_5.

Q. Write down industrial preparation of H_3PO_4.

Q. What is the effect of heat on orthophosphoric acid?

GROUP VIA ELEMENTS

Introduction

The members of group VIA are oxygen, sulphur, selenium, tellurium and polonium. These elements are called chalcogens, from the Greek for "copper giver", because they are often found in copper ores.

Electronic Configuration and Physical Properties of Group VIA Elements

Physical Properties	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Electronic configuration	$[He]2s^2 2p^4$	$[Ne]3s^2 3p^4$	$[Ar]4s^2 4p^4$	$[Kr]5s^2 5p^1$	$[Xe]6s^2 6p^4$
Ionization energy (kJ/mol)	1314	1000	941	869	813
Electron affinity (kJ/mol)	141.1	200.42	-195	-183	-180
Electronegativity	3.5	2.5	2.4	2.1	2.0
Atomic radius (pm)	66	104	117	137	152
Ionic radius 2-ion (pm)	140	184	198	221	---
Melting points (°C)	-218	113	217	450	254
Boiling points (°C)	-183	444.6	684	990	962
Density (g/cm^3)	0.00143	2.06	4.8	6.25	9.4

Q.13 Discuss the trends in physical properties of group VIA elements.

Ans. General characteristics of group VIA

(i) Nature of Elements

All the elements of group VIA are non-metals except Po which is a radioactive metal.

(ii) Periodicity in Physical properties

- Atomic radii, density, melting and boiling points generally increase with increase in atomic number down the group.

- Ionization energies of the group VIA members are very high which shows their reluctance to lose electrons.
- Oxygen is the most electronegative element (E.N=3.5) after fluorine.

(iii) Outermost Shell Electronic Configuration

The elements of VIA group have six electrons in their valance shell. Their outermost shell electronic configuration is ns^2np^4.

(iv) Allotropy

All the elements of group VIA show the property of allotropy.

- Oxygen has two allotropic forms (O_2 and O_3).
- Sulphur has 3 allotropes i.e. rhombic sulphur (α-sulphur), monoclinic sulphur (β-sulphur) and plastic sulphur (γ – sulphur).
- Se has two (red and gray) allotropes.
- Te has two (metallic and non metallic) allotropes.

(v) Valency

All the elements are polymeric in nature (they form poly-atomic molecules). They attain the electronic configuration of the nearest noble gas by gaining 2 electrons forming O^{-2}, S^{-2}, Se^{-2} etc.

(vi) Catenation

Self linking property of an element is called catenation. They also show the property of catenation. This property decreases down the group.

(vii) Covalency

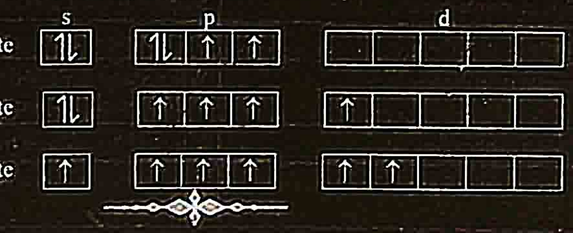
Except oxygen, the other members of the group VIA show a covalency of +2, +4 and +6, for example, $SC\ell_2$, $SC\ell_4$, $SC\ell_6$. +2 oxidation state is shown due to 2 unpaired electrons in the p-orbitals. +4 oxidation state is shown when 1 electron from p-orbital is promoted to the next vacant d-orbital, while +6 oxidation state is shown when another electron from s-orbital is also promoted to the next vacant d-orbital.

(viii) Polymeric molecule

The elements of this group usually form polymeric molecules. e.g. O_2, O_3, S_4, S_8 etc.

Q4. (iii) Why the elements of group VIA other than oxygen show more than two oxidation states?

Ans Except oxygen, the other members of group VIA show more than two oxidation states because they have empty d-orbitals. They show oxidation states +2, +4 and +6, for examples, SCl_2, SCl_4, SCl_6. +2 oxidation state is shown due to 2 unpaired electrons in the p-orbitals. +4 oxidation state is shown when 1 electron from "p" orbital is promoted to the next vacant d orbital; while +6 oxidation state is shown when one electron from p orbital and one electron from s orbital are promoted to the vacant d orbital.



Occurrence

Oxygen

- Oxygen is the most widely distributed and common of all the elements, comprising about 50% of the earth's crust.
- About one-fourth of the atmospheric air by weight consists of free oxygen, and water contains nearly 89% of combined oxygen.
- The calcium carbonate which occurs as chalk, lime stone, marble etc, contains 48% oxygen.
- Silica which is found in flint, quartz etc, contains more than 53% oxygen by weight.

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Sulphur

Sulphur is widely distributed in nature both as free and in combined forms.

Sulphides	Sulphates
galena (PbS)	gypsum ($CaSO_4$)
zinc blende (ZnS)	heavy spar ($BaSO_4$)
cinnabar (HgS)	
iron pyrite (FeS_2)	
stibnite (Sb_2S_3)	
copper pyrite ($Cu_2S.Fe_2S_3$)	

- Sulphur also occurs in organic compounds present in animals and vegetables. Onions, garlic, mustard, hair, many oils, eggs and proteins consist of compounds containing sulphur in them.
- It also occurs as a constituent of coal and petroleum.

Q4. (iv) Write down a comparison of the properties of oxygen and sulphur.

Ans: Comparison of Oxygen and Sulphur

Similarities

1. Both oxygen and sulphur have same outer electronic configuration of ns^2np^4.
2. Both oxygen and sulphur are usually divalent, O^{2-}, S^{2-}.
3. Both oxygen and sulphur exhibit allotropic forms. Allotropes of oxygen are O_3 and O_2 while allotropes of sulphur are, rhombic, monoclinic and plastic sulphur.
4. Both have polyatomic molecules. Oxygen has diatomic O_2 while sulphur has S_2 and S_8 molecules.
5. Both combine with metals in the form of O^{2-} and S^{2-} with oxidation state -2.
6. Both combine with non-metals and form covalent compounds, e.g, H_2O and H_2S, CO_2 and CS_2, etc.
7. Both are found in free and combined states on earth.
8. Both are typical non-metals.

Dissimilarities

Oxygen	Sulphur
1. There are two allotropic forms of oxygen i.e. O_2 and O_3.	There are 3 allotropic forms of sulphur i.e. rhombic, monoclinic and plastic.
2. It is gas at ordinary temperature.	It is solid at ordinary temperature.
3. Oxygen is sparingly soluble in water.	Sulphur is not soluble in water.
4. Oxygen helps in combustion.	Sulphur is itself combustible.
5. It is paramagnetic in nature.	It is diamagnetic in nature.
6. It does not react with water.	When steam is passed through boiling sulphur, a little hydrogen sulphide and sulphur dioxide are formed.
7. It does not react with acids.	It is readily oxidized by conc. sulphuric acid or nitric acid.
8. It does not react with alkalies.	It reacts with alkali solution and forms sulphides and thiosulphates.
9. It shows -2 oxidation state.	It shows oxidation states of -2, +2, +4 and +6.

SULPHURIC ACID H_2SO_4

Sulphuric acid was first prepared by a Muslim scientist Jabir Bin Hayyan in 8th century. In Europe, in 14th and 15th centuries, its preparation on commercial level was started due to the awareness of its properties and uses. It was called "oil of vitriol".

It does not occur as such in nature, however, small quantities of H_2SO_4 are found in the waters of some springs and rivers.

Sulphuric acid is also called **"King of chemicals"** and its production is a parameter for the industrial growth of a country.

Contact Process (Manufacture of sulphuric acid)

This method was developed by Knietsch in Germany. Basically, it involving the catalytic combination of sulphur and oxygen to form SO_2 which is then dissolved in water to form H_2SO_4.

Principle

SO_2 obtained by burning sulphur or iron pyrites is oxidized to SO_3 in the presence of V_2O_5 which acts as a catalyst. The best yield of SO_3 can be obtained by using excess of oxygen or air and keeping the temperature between 400 – 500°C. SO_3 formed is absorbed in concentrated H_2SO_4 and "Oleum" ($H_2S_2O_7$) formed can be converted to sulphuric acid of any strength by mixing adequate quantities of water.

Steps involved in contact process

The process is completed in steps given below:

(a) Sulphur burners

Sulphur or iron pyrites are burnt in excess of air to produce SO_2.

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$$

$$4FeS_{2(s)} + 11\,O_{2(g)} \longrightarrow 2Fe_2O_{3(s)} + 8\,SO_{2(g)}$$

Arsenic oxide may retard the catalytic ability of V_2O_5, so it must be removed.

(b) Purifying unit

SO_2 is purified from impurities like dust and arsenic oxide, to avoid poisoning of the catalyst. Purifying unit consists of the following parts.

(i) **Dust chamber:** Steam is injected to remove dust particles from the gases.

(ii) **Cooling pipes:** The gases are passed through lead pipes to cool them to 100°C.

(iii) **Scrubbers:** The cooled gases are washed by a spray of water, as SO_2 is not soluble in water at high temperature.

(iv) **Drying Tower:** The moisture of gases is removed by concentrated H_2SO_4 trickling down through the coke filled in this tower.

(v) **Arsenic Purifier:** Arsenic oxide is then removed by passing the gases through a chamber provided with shelves packed with freshly prepared ferric hydroxide.

(vi) **Testing box:** In this box, a beam of light is introduced which indicates the presence or absence of solid particles. If present the gases are sent back for further purification.

(c) Contact chamber

Pre-heated gases at 400-500°C are passed through vertical iron columns packed with the catalyst V_2O_5. Here SO_2 is oxidized to SO_3.

$$2SO_{2(g)} + O_{2(g)} \xrightarrow[V_2O_5]{400\text{-}500^\circ C} 2SO_{3(g)} \qquad \Delta H = -269.3 \text{ kJ/mol}$$

The reaction is highly exothermic so no heating is required once the reaction is started.

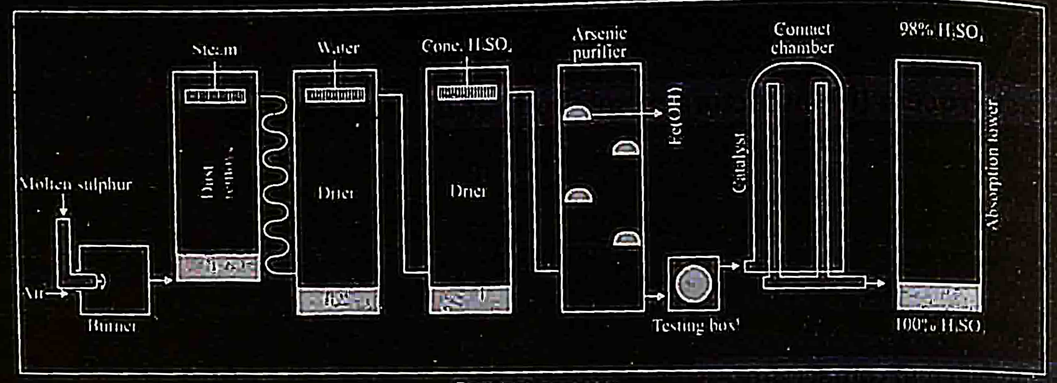
(d) Absorption Unit

The SO_3 obtained from the contact tower is dissolved in 98% H_2SO_4 to form "oleum" ($H_2S_2O_7$). It can be diluted with water to get any required concentration of sulphuric acid.

$$H_2SO_{4(aq)} + SO_{3(g)} \longrightarrow H_2S_2O_{7(\ell)}$$

$$H_2S_2O_{7(\ell)} + H_2O_{(\ell)} \longrightarrow 2H_2SO_{4(aq)}$$

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Contact process

Q.7 (b) Why is SO_3 dissolved in H_2SO_4 and not in water?

Ans When SO_3 is dissolved in 98% H_2SO_4, pyrosulphuric acid (oleum) is obtained.

$$H_2SO_{4(aq)} + SO_{3(g)} \longrightarrow H_2S_2O_{7(l)}$$

Oleum can be converted to sulphuric acid of any required concentration by mixing adequate amount of water.

$$H_2S_2O_{7(l)} + H_2O_{(l)} \longrightarrow 2H_2SO_{4(aq)}$$

While SO_3 is not dissolved in water directly because

(i) The reaction is highly exothermic.
(ii) SO_3 is less soluble in H_2O at high temperature.
(iii) A dense fog is produced which does not easily condense.
(iv) Sulphuric acid of required concentration cannot be prepared.

Q6. (b) Give the advantages of contact process for the manufacturing of sulphuric acis (H_2SO_4)

Ans The advantages of contact process for the manufacture of H_2SO_4 are given below:-

(i) By using this process, we can get H_2SO_4 of any required concentration.
(ii) As no by product is obtained during this process. So, it is a environment friendly process.
(iii) It is used in commercial preparations.
(iv) The catalyst used i.e. V_2O_5 is solid. So, it can be handled easily.

Physical Properties

1. Pure sulphuric acid is a colourless oily liquid without an odour.
2. Its specific gravity is 1.834 at 18°C.
3. It freezes at 10.5°C.
4. Its boiling point is 338°C.
5. It dissolves in water, liberating a lot of heat which raises the temperature of the mixture up to 120°C. H_2SO_4 should always be poured in water in a thin stream to avoid any accident.
6. Pure acid is a nonconductor of electricity but the addition of a little water makes it a good conductor.
7. It is extremely corrosive to skin and causes very serious burns to all the tissues.

Chemical Reactions

1. Decomposition

It is stable at ordinary temperature but on strong heating it dissociates into SO_3 and H_2O.

$$H_2SO_4 \longrightarrow SO_3 + H_2O$$

2. Dibasic acid

It is a strong acid. In an aqueous solution, it completely ionizes to give hydrogen, hydrogen sulphate and sulphate ions. The dissociation takes place in two steps.

$$H_2SO_{4(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(l)} + HSO^-_{4(aq)}$$

$$HSO^-_{4(aq)} + H_2O_{(l)} \longrightarrow SO^{2-}_{4(aq)} + H_3O^+_{(l)}$$

Q6. (a) Sulphuric acid is said to act as an acid, an oxidizing agent and a dehydrating agent, describe two reactions in each case to illustrate the truth of this statement.

Ans **Reactions of H_2SO_4 as an acid**

(i) Reactions with alkalies

$$H_2SO_{4(aq)} + NaOH_{(aq)} \longrightarrow NaHSO_{4(aq)} + H_2O_{(l)}$$

$$NaHSO_{4(aq)} + NaOH_{(aq)} \longrightarrow Na_2SO_{4(aq)} + H_2O_{(l)}$$

(ii) Reactions with carbonates and hydrogen carbonates:

$$Na_2CO_{3(aq)} + H_2SO_{4(aq)} \longrightarrow Na_2SO_{4(aq)} + H_2O_{(l)} + CO_{2(g)}$$

$$2NaHCO_{3(aq)} + H_2SO_{4(aq)} \longrightarrow Na_2SO_{4(aq)} + 2H_2O_{(l)} + 2CO_{2(g)}$$

(iii) Reactions with salts

$$2NaCl_{(s)} + H_2SO_{4(aq)} \xrightarrow{\text{strong heat}} Na_2SO_{4(aq)} + 2HCl_{(g)}$$

$$KNO_{3(aq)} + H_2SO_{4(aq)} \longrightarrow KHSO_{4(aq)} + HNO_{3(g)}$$

Q.7 (c) Explain the action of sulphuric acid on metals along with chemical equations?

Ans **Reactions of H_2SO_4 with Metals**

(a) Cold dilute acid reacts with almost all metals to produce hydrogen gas.

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

$$Mg + H_2SO_4 \longrightarrow MgSO_4 + H_2$$

$$Sn + H_2SO_4 \longrightarrow SnSO_4 + H_2$$

(b) Cold concentrated H_2SO_4 does not react with most of the metals like Cu, Ag, Hg, Pb, Au.

(c) With certain metals, hot concentrated sulphuric acid gives metal sulphates, water and SO_2.

$$Cu_{(aq)} + 2H_2SO_{4(aq)} \longrightarrow CuSO_{4(aq)} + 2H_2O_{(aq)} + SO_{2(aq)}$$

$$2Ag_{(aq)} + 2H_2SO_{4(aq)} \longrightarrow Ag_2SO_{4(aq)} + 2H_2O_{(aq)} + SO_{2(aq)}$$

$$Hg_{(l)} + 2H_2SO_{4(aq)} \longrightarrow HgSO_{4(aq)} + 2H_2O_{(l)} + SO_{2(aq)}$$

Q4.(v) Write down the equation for the reaction between conc. H_2SO_4 and copper and explain what type of reaction is it.

Ans **Reaction between conc. H_2SO_4 and copper:**

Hot conc. sulphuric acid reacts with Cu to form copper sulphate and SO_2.

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$$Cu^{0} + 2H_2S^{+6}O_4 \longrightarrow Cu^{+2}SO_4 + 2H_2O + S^{+4}O_2$$

Oxidation

Reduction

In this reaction, the oxidation state of Cu is changed from "zero" to "2" in $CuSO_4$ and thus Cu is oxidized. The oxidation state of S in H_2SO_4 is +6 whereas in SO_2 it is +4. This shows that sulphur is reduced. Therefore the reaction is an oxidation reduction.

Reactions as a dehydrating agent

H_2SO_4 has a great affinity for water, so it acts as dehydrating agent and eliminates water from different compounds.

(i) With oxalic acid it forms CO_2 and CO.

$$\begin{matrix}COOH\\|\\COOH\end{matrix} \xrightarrow{\text{conc } H_2SO_4} CO_{2(g)} + CO_{(g)} + H_2O_{(\ell)}$$

(ii) With formic acid, CO is formed.

$$HCOOH_{(aq)} \xrightarrow{\text{conc } H_2SO_4} CO_{(g)} + H_2O_{(\ell)}$$

(iii) With ethyl alcohol it forms ethylene or ethene.

$$C_2H_5OH \xrightarrow[100°C]{\text{conc } H_2SO_4} C_2H_4 + H_2O$$

(iv) With wood, paper, sugar and starch it forms carbon and water.

$$C_6H_{12}O_6 \xrightarrow{\text{conc } H_2SO_4} 6C + 6H_2O$$

$$C_{12}H_{22}O_{11} \xrightarrow{\text{conc } H_2SO_4} 12C + 11H_2O$$

$$(C_6H_{10}O_5)n \xrightarrow{\text{conc } H_2SO_4} 6nC + 5nH_2O$$

Q. What happens when conc. H_2SO_4 is treated with
(i) Ethyl Alcohol
(ii) Sugar
(iii) Starch

As an Oxidizing Agent

H_2SO_4 acts as a strong oxidizing agent.

(i) It oxidizes C and S giving CO_2 and SO_2 respectively.

$$C_{(s)} + 2H_2SO_{4(aq)} \longrightarrow CO_{2(g)} + 2SO_{2(g)} + 2H_2O_{(g)}$$

$$S_{(s)} + 2H_2SO_{4(aq)} \longrightarrow 3SO_{2(g)} + 2H_2O_{(\ell)}$$

(ii) H_2S is oxidized to S.

$$H_2S_{(g)} + H_2SO_{4(aq)} \longrightarrow S_{(s)} + SO_{2(g)} + 2H_2O_{(g)}$$

(iii) Reactions of H_2SO_4 with HBr and HI produce bromine and iodine respectively.

$$2HBr_{(aq)} + H_2SO_{4(aq)} \longrightarrow Br_{2(g)} + SO_{2(g)} + 2H_2O_{(g)}$$

$$2HI_{(aq)} + H_2SO_{4(aq)} \longrightarrow I_{2(g)} + SO_{2(g)} + 2H_2O_{(g)}$$

Reactions with Gases

(i) It absorbs SO_3 and forms oleum.

$$H_2SO_{4(aq)} + SO_{3(g)} \longrightarrow H_2S_2O_{7(\ell)}$$

(ii) It reacts with ammonia forming ammonium sulphate.

$$2NH_{3(g)} + H_2SO_{4(aq)} \longrightarrow (NH_4)_2SO_{4(aq)}$$

Q. Which of the following gas cannot be dried with sulphuric acid?
(a) CO (b) CO_2
(c) NH_3 (d) O_2

Reaction with Benzene

Benzene sulphonic acid is produced when H_2SO_4 reacts with benzene.

$$C_6H_{6(\ell)} + H_2SO_{4(aq)} \longrightarrow \underset{\text{Benzene sulphonic acid}}{C_6H_5SO_2OH_{(\ell)}} + H_2O_{(\ell)}$$

Precipitation Reactions

White precipitates is produced when H_2SO_4 reacts with aqueous solutions of $BaCl_2$, $Pb(NO_3)_2$ and $Sr(NO_3)_2$.

$$BaCl_{2(aq)} + H_2SO_{4(aq)} \longrightarrow BaSO_4\downarrow + 2HCl_{(aq)}$$

$$Pb(NO_3)_{2(aq)} + H_2SO_{4(aq)} \longrightarrow PbSO_4\downarrow + 2HNO_{3(aq)}$$

Reactions with Oxidizing Agents

It reacts with oxidizing agents like $KMnO_4$ and $K_2Cr_2O_7$ to liberate oxygen which may oxidize other compounds.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$10FeSO_4 + 5H_2SO_4 + 5[O] \longrightarrow 5Fe_2(SO_4)_3 + 5H_2O$$

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

Uses of Sulphuric Acid

It is used:

1. in the manufacture of fertilizers like ammonium sulphate $(NH_4)_2SO_4$ and calcium superphosphate $Ca(H_2PO_4)_2$.
2. in refining of petroleum to remove nitrogen and sulphur compounds.
3. in the manufacture of HCl, H_3PO_4, HNO_3, and sulphates.
4. as a dehydrating agent for drying gases.
5. in electrical batteries and storage cells.
6. in the manufacture of many chemicals, dyes, drugs, plastics, disinfectants, paints, explosives, synthetic fibers etc.
7. as a laboratory reagent.
8. in textile, iron, steel, leather and paper industries.

KEY POINTS

1. In group V-A the metallic character increases down the group. Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids while bismuth is a metal.
2. Phosphorus and other members of V-A group can make use of d-orbitals in bonding.
3. Common oxides of nitrogen are N_2O, NO, NO_2, N_2O_3 and N_2O_5.
4. Nitrogen forms two oxyacids, HNO_2 and HNO_3, HNO_2 is an unstable acid and exists only in solution.
5. HNO_3 is not only a strong acid but it also acts as a strong oxidizing agent.
6. Aqua regia is a mixture of one volume of concentrated HNO_3 and three volumes of concentrated HCl.
7. Phosphorus exists in six allotropic forms. White phosphorus is very reactive as compared to red phosphorus.
8. Phosphorus forms two types of chlorides PCl_3, PCl_5 and two types of oxides P_2O_3 and P_2O_5 oxides.
9. Just like nitrogen, phosphorus also gives two types of oxyacids: phosphorus acid (H_3PO_3) and phosphoric acid (H_3PO_4).
10. Phosphoric acid is a weak tribasic acid and it gives three series of salts with strong bases.
11. Group VI-A of the periodic table contains only one metal, polonium, the rest of members are non-metals. All these elements show the property allotropy and they are polymeric in nature.
12. Oxygen and sulphur are the most abundant elements of group VI-A. Oxygen is the most widely distributed and common of all the elements. Sulphur is widely distributed in nature in both free and combined forms.
13. Sulphuric acid is commercially prepared by oxidation of SO_2 in the presence of a catalyst to SO_3 in a process called Contact Process.
14. H_2SO_4 is a very strong acid. It acts as a dehydrating agent as well as an oxidizing agent.

SOLVED OBJECTIVE EXERCISE

Q1. Fill in the blanks.
(i) The elements _____ of group VA are called metalloids
(ii) In Birkeland and Eyde's process _____ is prepared from atmospheric oxygen and nitrogen.
(iii) The tendency to form long chain of atoms is called _____.

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(iv) All the elements of group VIA show the property of _____.
(v) Selenium shows two allotropic forms which are called _____ forms.
(vi) Specific gravity of H_2SO_4 at 18°C is _____.
(vii) H_2 is produced by reacting H_2SO_4 with metals, like _____.
(viii) The elements of group VA exhibit maximum oxidation state of _____.
(ix) The outermost shell of group _____ elements contain six electrons.
(x) Oxygen shows _____ behaviour due to the presence of unpaired electrons.
(xi) Conc. Phosphoric acid acts as a _____.
(xii) Nitrogen is gas while other elements of the same group are _____.
(xiii) Noble metals like gold and platinum are dissolved in _____.
(xiv) Sulphur is different from oxygen because it shows _____ oxidation states.
(xv) HNO_3 is used in the manufacture of _____ fertilizers.

Answer Key.

(i)	Arsenic & Antimony	(ii)	(NO) nitric oxide
(iii)	Catenation	(iv)	Allotropy
(v)	Red and grey	(vi)	1.834
(vii)	Fe, Mg, Zn, Sn	(viii)	+5
(ix)	VI-A	(x)	Paramagnetic
(xi)	Deliquescent	(xii)	Solid
(xiii)	Aqua Regia	(xiv)	Variable
(xv)	Nitrogeneous		

Q2. Indicate True or False.

(i) The metallic character in groups VA and VIA elements increases down the group.
(ii) The elements of group VA exhibit maximum oxidation state of + 5.
(iii) Ionization energy of phoshorus is greater than that of nitrogen.
(iv) The electronegativity of oxygen is greater than all other elements of groups VA and VIA.
(v) V_2O_5 is used as a catalyst for the oxidation of SO_2 to SO_3.
(vi) The oxides of nitrogen are basic in nature.
(vii) Aqua regia is prepared by mixing 3 parts of conc. HNO_3 with one part of conc. HCl.
(viii) TNT is prepared by the reaction of nitric acid with toluene.
(ix) P_2O_3 when reacts with cold water gives phosphorus acid and with hot water it gives phosphoric acid.
(x) Sulphur occurs in many organic compounds of animal and vegetable origins.

Answer Key.

(i)	True	(ii)	True	(iii)	False	(iv)	True	(v)	True
(vi)	False	(vii)	False	(viii)	True	(ix)	True	(x)	True

Q3. Multiple choice questions. Encircle the correct answer.

(i) Out of all the elements of group VA, the highest ionization energy is possessed by.
(a) N (b) P (c) Sb (d) Bi

(ii) Among group VA elements, the most electronegative elements is
(a) Sb (b) N (c) P (d) As

(iii) Oxidation of NO in air produces
(a) N_2O (b) N_2O_3 (c) N_2O_4 (d) N_2O_5

(iv) The brown gas formed, when metal reduces HNO_3 to
(a) N_2O_4 (b) N_2O_3 (c) NO_2 (d) NO

(v) Laughing gas is chemically
(a) NO (b) N_2O (c) NO_2 (d) N_2O_4

(vi) Out of all the elements of group VIA, the highest melting and boiling points is shown by the element.
(a) Te (b) Se (c) S (d) Pb

(vii) SO_3 is not absorbed in water directly to form H_2SO_4 because
(a) The reaction does not go to completion. (b) The reaction is quite slow.
(c) The reaction is highly exothermic. (d) SO_3 is insoluble in water.

(viii) Which catalyst is used in contact process?
(a) Fe_2O_3 (b) V_2O_5 (c) SO_3 (d) Ag_2O

(ix) Which of the following specie has the maximum number of unpaired electrons?
(a) O_2 (b) O_2^+ (c) O_2^- (d) O_2^{2-}

Solved Exercise MCQ's

Q. No	Answer	Reason
(i)	(a) N	Size of N is smallest than other elements of its group. Due to small size, it is very difficult to remove an electron from its outermost shell, that's why it has highest ionization energy.
(ii)	(b) N	Electrongativity decreases down the group.
(iii)	(c) N_2O_4	$2NO + O_2 \longrightarrow 2NO_2$ $\Rightarrow$ NO_2 gas exists in N_2O_4 state (dimer)
(iv)	(c) NO_2	$Cu_{(s)} + 4HNO_{3(conc.)} \longrightarrow Cu(NO_3)_{(conc.)} + 2NO_{2(g)} + 2H_2O_{(l)}$ $\Rightarrow$ NO_2 gas is reddish brown in color.
(v)	(b) N_2O	Its mixture with little oxygen, if inhaled for sufficiently long time causes hysterical laughter.
(vi)	(a) Te	The melting and boiling point increases down the group among non-metals. So, Te has highest melting (450°C) and boiling point (990°C).
(vii)	(c) The reaction is highly exothermic.	The reaction of SO_3 and water is highly exothermic as heat contents of reactants is higher than that of product (H_2SO_4)
(viii)	(b) V_2O_5	V_2O_5 is very effective catalyst for the conversion of SO_2 to SO_3 gas.
(ix)	(a) O_2	No. of unpaired electrons in O_2 = 2 No. of unpaired electrons in O_2^+ = 1 No. of unpaired electrons in O_2^{+2} = 0 No. of unpaired electrons in O_2^- = 1 No. of unpaired electrons in O_2^{-2} = 0

Previous Board Questions

1. HNO_3 is Oxidizing Agent, justify by equations.
2. P_2O_5 is powerful dehydrating agent. Prove by examples.
3. What is laughing Gas? Why is it called so?
4. How many allotropic forms of phosphorus exist? Write the name of any three forms.
5. Justify that "NO" acts as reducing agent.
6. What is meant by Fuming of nitric acid?
7. How does nitrogen differ from other members of its family?
8. Why is SO_3 dissolved in H_2SO_4 and not in water?

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9. What is allotropy? Name the different allotropes of phosphorus.
10. Explain the electron dot structure of nitrous acid and nitric acid.
11. Give the reactions of dilute nitric acid with
    (a) Magnesium (b) Copper
12. Describe ring test for the confirmation of the presence of nitrate ions in solution
13. Write down the uses of sulphuric acid.
14. What is the heating effect on orthophosphoric acid?
15. Write down dissimilarities between oxygen and sulphur.
16. How does HNO_2 act as a reducing agent?
17. Give reaction of HNO_3 with
    (a) As (b) Sb
18. Give four uses of HNO_3.
19. Give reactions in which H_2SO_4 oxidizes
    (a) Carbon (b) H_2O
20. Why does Aqua Regia dissolve gold and platinum?
21. Why elements of group VIA other than oxygen show move than two oxidation states?
22. H_2SO_4 is a strong dehydrating agent. Give examples.
23. Reactions of P_2O_3 and P_2O_5 with cold and hot water.

For Answers study

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CHAPTER 5

THE HALOGENS AND NOBLE GASES

Introduction

- The elements fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At) are called halogens.
- These elements are called the halogens from Greek hals, "salt" and gennan, "to form or generate", because they are literally the salt formers.
- The halogen elements form a group of very reactive non-metals and are quite similar to each other in their chemical properties.
- First four elements are the common elements of the halogen family
- Astatine is a rare halogen. It is radioactive and its most stable isotope has a half life of 8.3 hrs.

Physical Properties

(i) Physical state

Halogens exist as discrete diatomic molecules in all phases (gas, liquid or solid).

- Fluorine and chlorine are gases of pale yellow and greenish yellow colours respectively at room temperature and pressure.
- Bromine is a liquid of red-brown colour.
- Iodine is a metallic-appearing shiny grayish black solid.

(ii) Odour

The halogens have irritating odours, and they attack the skin. Bromine in particular causes burns that heal slowly.

(iii) Outer shell electronic configuration

The outer shell of halogens have the configuration ns^2np^5 (one electron short of the stable octet of the noble gases).

(iv) Ionization energy

The ionization energy data of the halogens show that the fluorine atom holds its electrons tightly whereas the electrons are least tightly bound in iodine. The trend can be correlated with the sizes of the halogen atoms.

(v) Electron affinity

The electron affinity values of halogens are large and negative, that is why halogens gain electrons readily. They have large, positive standard electrode potentials and their electronegativities are also fairly high.

(vi) Intermolecular forces

The intermolecular attraction is greater in the larger molecules having greater masses. Due to their large size the van der Waals's forces in iodine molecules are stronger than in the smaller molecules of the other halogens.

The Electronic Configurations and the Important Physical Properties of the Halogens

Properties	Fluorine	Chlorine	Bromine	Iodine
Atomic number	9	17	35	53
Electronic configuration	$[He]2s^22p^5$	$[Ne]3s^23p^5$	$[Ar]3d^{10},4s^2,4p^5$	$[Kr]4d^{10},5s^2,5p^5$
Physical appearance	Pale yellow gas	Greenish yellow gas	Red-brown liquid	Shiny grayish black solid
Ionization energy ($kJmol^{-1}$)	1681	1251	1140	1008

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Electron affinity, ($kJmol^{-1}$)	-322	-349	-325	-295
Electronegativity	4.00	3.00	2.8	2.5
Ionic radius (pm)	136	181	196	216
Covalent radius (pm)	72	99	114	133
Melting point (°C)	-220	-101	-7.2	114
Boiling point (°C)	-188	-34.6	58.8	184.4
Density (g/cm^3)	0.00181	0.00321	3.12	4.93
Oxidation states	-1	-1,+1,+3,+5,+7	-1,1,+3,+5,+7	-1,1,+3,+5,+7
Bond energy ($kJmol^{-1}$) (X-X)	154.80	242.67	192.46	150.6

OCCURRENCE

Electronegativity Value and Existence of Element

Elements with the higher values of electronegativity usually exist as negative ions, and those with the lower values of electronegativity exist as positive ions. Elements with intermediate values of electronegativity are often found as ions or molecules or in free (elemental) form.

Existence of Halogens

- None of the halogens is found in free form in nature.
- The halogens exist in nature primarily in the form of compounds.
- Their most common state is the halide ions F^-, Cl^-, Br^- and I^-.
- These halides are soluble in water and are found in sea, in salt lakes and as underground beds of salt.

Fluorine	Chlorine	Bromine	Iodine
Fluorspar CaF_2	Halite NaCl (Salt beds, brine wells, sea water)	Brine wells, sea water, NaBr, KBr, $MgBr_2$	$NaIO_3$, $NaIO_4$ deposits in Chile brine wells.
Cryolite Na_3AlF_6	Carnallite KCl. $MgCl_2.6H_2O$		
Fluoroapatite $Ca_5(PO_4)_3F$			

Q.13 (iii) Arrange the following ions in order of increasing size:

F^-, Cl^-, I^-, Br^-

Ans In a group, ionic radii is in increasing order from top to bottom with the increase in number of shells and shielding effect and decrease of attractions of electrons towards nucleus. Fluorine is present at the top of VII-A group and its ion (F^-) is smaller as compare to the size of I^- ion.

Thus, the arrangement of given ions in increasing order is

$$F^- < Cl^- < Br^- < I^-$$

Q.13 (iv) Why iodine has metallic luster?

Ans Metallic Luster of iodine is due to the excitation and then de-excitation of valence electrons. Due to bigger size of iodine molecule valence electrons experience weak nuclear attraction. When light falls on iodine surface weakly bounded valence electrons by absorbing energy go into excited state. These excited electrons when de-excite they emit energy in the form of radiations. These radiations give greyish-black metallic luster to iodine.

Q.13 (v) Which halogen sublimes to violet vapours?

Ans "A substance which upon heating directly converts into vapours without passing through liquid phase is called sublime substance."

Among halogens F_2 and Cl_2 are gases at room temperature, Br_2 a liquid and I_2 exists as a solid. Due to having weak intermolecular forces, iodine directly converts into violet vapours on heating.

Peculiar Behaviour of Fluorine

The halogens form a homologous series but fluorine differs from the other halogens in many respects which is due to:

(i) Small size of F atom and F^- ion. (F = 72pm, F^- = 136pm)
- Better overlapping of orbitals, results in formation of strong and short bond with elements other than O, N and itself.

(ii) High first ionization energy and electronegativity. (I.E = 1681$kJmol^{-1}$, E.N = 4.00)

(iii) Low dissociation energy of F_2 as compared to Cl_2 and Br_2. (F-F = 154.80 $kJmol^{-1}$, Cl-Cl =242.67 $kJmol^{-1}$)
- Due to low dissociation energy, F_2 is highly reactive than Cl_2 and Br_2.

(iv) Restriction of valence shell to an octet.
- Due to restriction of the valence shell to an octet, many fluoro compounds show inertness e.g., CF_4, SF_6, SiF_4. Also due to this restriction, fluorine remains restricted to -1 oxidation state.

(v) Fluorine is the only element that combines directly with noble gases like Kr, Xe, and Rn forming their fluorides.

(vi) Ionic fluorides have higher lattice energies than the other halides and these values are responsible for the insolubility of the fluorides of Ca, Mg, Ba, Sr and lanthanides in water. The fluorides are, however, more stable with respect to dissociation into elements.

Oxidizing Properties

- All the free halogens (F_2, Cl_2, Br_2, I_2) act as oxidizing agents when they react with metals or non-metals. The reactant elements acquire positive oxidation state in compound form.
- On forming ionic compounds with metals, the halogen gain electrons and are converted into negative halide ions.

$$2Na + Cl_2 \longrightarrow 2Na^+Cl^-$$

Relative Reactivities of the Halogens as Oxidizing Agents

The oxidizing power of halogens decreases with increase in atomic number. Fluorine has the highest oxidizing power and iodine the least. The order of decreasing power as an oxidizing agent is:

$$F_2 > Cl_2 > Br_2 > I_2$$

The oxidizing power of halogens depends upon the following factors:

(i) Energy of dissociation
(ii) Electron affinities of atoms
(iii) Hydration energies of ions
(iv) Heats of vaporization (for Br_2 and I_2)

If a halogen has low energy of dissociation, a high electron affinity and a higher hydration energy of its ions it will have a high oxidizing power. e.g. Oxidizing power of F_2 is higher because it has low energy of dissociation and higher hydration energy of its ions.

Relative reactivites

Due to the relative strength as oxidizing agents, it is possible for each free halogen to oxidize the ions of other halogens next to it, in the family. Standard electrode potential measures oxidizing power.

Electrode potential:
It is relative tendency of the electrode to oxidize or reduce the standard hydrogen electrode.

Standard reduction potential. E^o (V) $X_2 + 2e^- \longrightarrow 2X^-$	F_2	Cl_2	Br_2	I_2
	+2.87	+1.36	+1.07	+0.54

- Fluorine can oxidize all the halide ions to molecular halogens. (A reaction will occur if the value of $E°$ is positive).

$$F_2 + 2e^- \longrightarrow 2F^- \qquad E° = 2.87V$$
$$2Cl^- \longrightarrow Cl_2 + 2e^- \qquad E° = -1.36V$$
$$F_2 + 2Cl^- \longrightarrow Cl_2 + 2F^- \qquad E° = +1.51V$$

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- In the similar way, chlorine will oxidize both bromide and iodide ions, while bromine can oxidize only iodide ion.

$$Cl_2 + 2Br^- \longrightarrow Br_2 + 2Cl^-$$

$$Br_2 + 2I^- \longrightarrow I_2 + 2Br^-$$

Q. Why fluorine has higher oxidizing properties?

- Iodine being a weak oxidizing agent cannot oxidize chloride or bromide ion.

Application

Fluorine and chlorine can oxidize various coloured dyes to colourless substances. Colour of litmus or universal indicator can be decolourized when exposed to fluorine or chlorine. When chlorine acts as bleaching agent, it behaves as oxidizing agent.

Compounds of Halogens

Hydrogen Halides (HX)

Hydrogen halides are HF, HCl, HBr and HI

Preparations

1. Direct combination with hydrogen

All halogens react with hydrogen to form hydrogen halides, e.g.,

$$H_2 + F_2 \longrightarrow 2HF$$

$$H_2 + Cl_2 \longrightarrow 2HCl$$

$$H_2 + Br_2 \longrightarrow 2HBr$$

$$H_2 + I_2 \longrightarrow 2HI$$

- The reaction of molecular hydrogen and fluorine is very fast and explosive.
- With chlorine, molecular hydrogen reacts in the presence of sunlight.
- Bromine and iodine react with molecular hydrogen at a higher temperature. The reaction with iodine is very slow and reversible.

Direct combination is used as a preparative method only for HCl and HBr.

2. Reaction of conc. H_2SO_4 with halides

Hydrogen fluoride and hydrogen chloride can also be obtained by the action of concentrated sulphuric acid on fluorides and chlorides, but analogous reactions with bromides and iodides result in partial oxidation of the hydrogen halide to the free halogen.

$$2NaCl_{(s)} + H_2SO_{4(conc.)} \longrightarrow Na_2SO_{4(aq)} + 2HCl_{(g)}$$

$$2NaBr_{(s)} + 2H_2SO_{4(conc.)} \longrightarrow Na_2SO_{4(aq)} + Br_{2(\ell)} + SO_{2(g)} + 2H_2O_{(\ell)}$$

$$2NaI_{(s)} + 2H_2SO_{4(conc.)} \longrightarrow Na_2SO_{4(aq)} + I_{2(s)} + SO_{2(g)} + 2H_2O_{(\ell)}$$

It turns starch paper blue.

Q. Write down the properties of HF.

Ans

Properties of HF:

(i) It is a highly volatile liquid, having boiling point 19.5°C.

(ii) HF attacks glass and has found applications as a non-aqueous solvent.

(iii) It can be handled in Teflon. If HF is absolutely dry, it can be stored in copper or stainless steel container kept under vacuum.

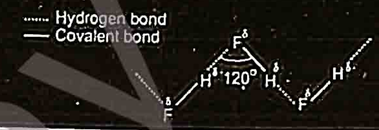
(iv) Pure liquid HF is strongly hydrogen bonded and is a viscous liquid but its viscosity is less than water.

(v) In vapour phase, H – bond is responsible for HF molecule. Various test results indicate that gaseous HF consists of an equilibrium mixture of monomers and cyclic hexamers.

$$6HF \rightleftharpoons (HF)_6$$

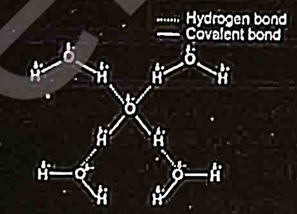
(vi) Chain polymers may also exist under certain conditions. Chains and rings of HF are of various sizes, some of these persist in the vapour phase as well.

(vii) Due to strong HF bond, it is a weak reducing agent.

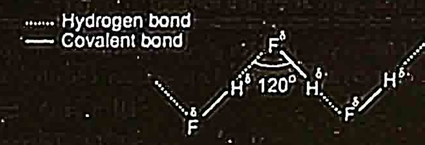


Q. HF is less viscous than water? Justify?

Ans The viscosity of a liquid mainly depends upon the strength of intermolecular forces, the shape and size of molecules. In water, two H-bonding per molecule are present. Moreover water has a three dimensional network of hydrogen bonds. On the other hand, in HF, there is one hydrogen bond per molecule and the absence of three dimensional network of hydrogen bonds.



Hydrogen bonding in water



Conclusion: It shows that stronger intermolecular forces and large three dimensional structure makes water more viscous than HF.

Q. Write down physical properties of hydrogen halides.

Ans

Properties of Hydrogen Halides

(i) HF is a colourless volatile liquid whereas other hydrogen halides (HCl, HBr, HI) are colourless gases at room temperature. They give fumes in moist air. They are strong irritants.

(ii) Melting points, boiling points, heats of fusion and heats of vapourization increase regularly from HCl to HI. The HF has much higher values for these properties due to hydrogen bonding. A very high boiling point of hydrogen fluoride is a major evidence of the presence of hydrogen bonding among its molecules. The relative volatility of HCl, HBr and HI reflects the strengthening of the van der Waal's forces due to increasing size of halogens. Since the dipole moment of molecules decreases from HCl to HI, probably dipole-induced dipole forces play an important role in the intermolecular binding of the heavier HX molecules.

(iii) The strength of the hydrogen halogen bond is very high in HF. It decreases with increasing size of the halogen atom. The bond strength is reflected in the ease of dissociation of hydrogen halides at elevated temperatures.

(iv) HF, HCl, HBr and HI act as reducing agents in the following order:

$$HF < HCl < HBr < HI$$

Hydrogen iodide is a strong reducing agent. In redox reactions, the hydrogen halides are oxidized to elemental halogens. e.g.

$$2HI + S \rightleftharpoons I_2 + H_2S$$

(v) In water, hydrogen halides give hydrofluoric, hydrochloric, hydrobromic and hydroiodic acids. Hydrofluoric acid is a weak acid due to limited ionization. The other three acids are very strong acids:

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$

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$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

The strength of acids increases in the order of:

$$HF < HCl < HBr < HI$$

Some Physical Properties of Hydrogen Halides

Property	HF	HCl	HBr	HI
Melting points (°C)	-83.8	-114.2	-86.9	-50.8
Boiling points (°C)	19.5	-85.0	-66.7	-35.3
Heat of fusion at M.P. (kj/mol)	4.58	1.99	2.41	2.87
Heat of vapourization at B.P. (kJ/mol)	30.3	16.2	17.6	19.7
Heat of formation / kJ mol^{-1} (ΔH_f)	-270.0	-92.0	-36.0	+26.0
Bond energy (kJ $/mol^{-1}$)	566	431	366	299
H – X Bond length (pm)	92	128	141	160
Dissociation into elements at 1000°C (%)	0	0.014	0.5	33
Dipole moment (Debye)	1.8	1.1	0.8	0.4

Q.7 (a) How the halogen acids are ionized in water?

Ans In water, hydrogen halides give hydrofluoric, hydrochloric, hydrobromic and hydroiodic acids. Hydrofluoric acid is a weak acid due to limited ionization. The other three acids are very strong acids.

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

The strength of acids increases in the order of:

$$HF < HCl < HBr < HI$$

HF is the weakest acid and HI is the strongest acid.

Q.7 (b) Why HF is weaker acid than HCl?

Ans

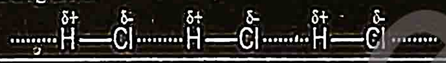
HF is a weaker acid than HCl

A substance which has a tendency to give proton (H^+) in an aqueous solution is called acid. The strength of an acid is directly proportional to its proton (H^+) releasing power.

In HF strong hydrogen bonding is present and partially positive hydrogen is entrapped between two strong electronegative fluorine atoms.

Consequently it becomes difficult for proton to be ionized in water which makes it weak acid.

On the other hand in HCl dipole-dipole interaction is present which is weaker than hydrogen bonding. Therefore proton (H^+) releasing power of HCl is more which makes it strong acid.



Q. Hydrogen halides act as reducing agents. Justify?

Ans

Hydrogen halides as reducing agents

HF, HCl, HBr and HI act as reducing agents in the following order:

$$HF < HCl < HBr < HI$$

Hydrogen iodide is a strong reducing agent. In redox reactions, the hydrogen halides are oxidized to element all halogens. e.g.

$$2HI + S \longrightarrow I_2 + H_2S$$

Oxides of Halogens

"The compounds which contain oxygen and halogens chemically combined together are called oxides of halogens."

The halogens do not react directly with oxygen. With the help of some indirect methods, following oxides of group VIIA elements have been made:

Oxides of Halogen

Fluorine	Chlorine	Bromine	Iodine
Oxygen difluoride, OF_2	Dichlorine monoxide, Cl_2O	Bromine monoxide, Br_2O	Iodine tetraoxide, I_2O_4
Dioxygen difluoride, O_2F_2	Chlorine dioxide, ClO_2	Bromine dioxide, BrO_2	Iodine iodate, I_4O_9
Trioxygen difluoride, O_3F_2	Chorine hexaoxide, Cl_2O_6	Bromine trioxide, BrO_3, (Br_3O_8)	Iodine pentoxide, I_2O_5
-	Chlorine heptaoxide, Cl_2O_7	-	-

Oxides of Flourine

Trioxygen Difluoride (O_3F_2)

Preparation: This oxide can be prepared when a mixture of fluorine and oxygen is subjected to electric discharge.

$$2F_2 + 3O_2 \longrightarrow 2O_3F_2$$

Colour variation: At 363°C, it is a dark red viscous liquid but turns to reddish brown solid at 350°C.

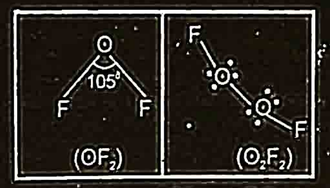
Decomposition: On decomposition, it gives oxygen and other oxide of fluorine.

$$2O_3F_2 \longrightarrow 2O_2F_2 + O_2$$

Reaction with F_2: O_3F_2 reacts with F_2 in the presence of electric discharge to produce O_2F_2.

$$2O_3F_2 + F_2 \longrightarrow 3O_2F_2$$

Structure of OF_2 and O_2F_2:



Structures of OF_2 and O_2F_2

Q.5 (a) Discuss the oxides of chlorine.

Oxides of Chlorine

- The oxides of chlorine are generally unstable.
- It is not possible to synthesize them by direct combination of the elements Cl_2 and O_2.
- They have extensive industrial use as
  - (i) commercial bleaching agents for wood, paper-pulp.
  - (ii) for water treatment.

1. Chlorine Dioxide ClO_2

Preparations

(i) It is prepared by reducing $NaClO_3$ with NaCl or SO_2 or CH_3OH in strongly acidic solution.

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$$2ClO_3^- + 2Cl^- + 4H^+ \longrightarrow 2ClO_2 + Cl_2 + 2H_2O$$

(ii) ClO_2 can also be prepared by the action of concentrated H_2SO_4 on $KClO_3$. This reaction is violent. To control the reaction, oxalic acid should be added.

$$2KClO_3 + H_2C_2O_4 + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O + 2CO_2 + 2ClO_2$$

Properties

- It is a pale yellow gas.
- ClO_2 explodes into Cl_2 and O_2 on warming.
- It is soluble in water and is stable in dark.
- It decomposes slowly in H_2O to HCl and $HClO_3$.
- It is a paramagnetic substance.

Uses: It is used as:

(i) an antiseptic.
(ii) for purification of water.
(iii) to bleach cellulose material.

2. Chlorine [illegible] (Cl_2O_7)

chloric acid ($HClO_4$).

Preparation

It can be obtained at –10°C by dehydration of $HClO_4$ with P_2O_5.

$$2HClO_4 + P_2O_5 \xrightarrow{-10°C} Cl_2O_7 + 2HPO_3$$

Oxides of Bromine

Oxides of bromine are dark volatile liquids with low thermal stability.

Bromine Monoxide (Br_2O)

Preparation

(i) It can be prepared by the reaction of bromine vapours with mercuric oxide.

$$HgO + 2Br_2 \xrightarrow{50°C} HgBr_2 + Br_2O$$

(ii) Br_2O can also be prepared by treating the suspension of mercuric oxide in CCl_4 with bromine.

Properties

- It is stable in dark in CCl_4 at –20°C.
- It has oxidizing properties.

Oxides of Iodine

Out of all the oxides of iodine only iodine pentoxide I_2O_5 is important. The other compounds, I_2O_4 and I_4O_9 are salt like and are considered as iodine-iodates.

Iodine Pentoxide (I_2O_5)

Preparation

It can be prepared by heating iodic acid at 240°C.

$$2HIO_3 \xrightarrow{240°C} I_2O_5 + H_2O$$

Properties

- It is a white crystalline solid, stable up to 300°C.
- It has a polymeric structure.
- It is insoluble in organic solvents.
- It forms iodic acid with water. $I_2O_5 + H_2O \longrightarrow 2HIO_3$
- It reacts with H_2S, HCl and CO and acts as an oxidizing agent.

Use: It is used for the quantitative analysis of CO.

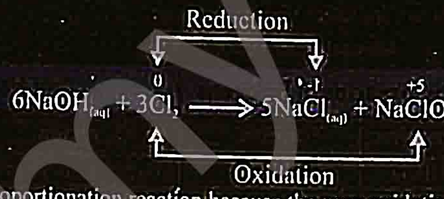
$$5CO + I_2O_5 \longrightarrow I_2 + 5CO_2$$

Q.5 (b) What are disproportionation reactions? Explain your answer with an example.

Ans **Disproportionation Reaction**

"A reaction in which a species (molecule, atom or ion) is simultaneously oxidized and reduced is called disproportionation reaction".

Example:



This reaction is a disproportionation reaction because the zero oxidation state of chlorine atom in Cl_2 is converted to –1 in chloride and +5 in chlorate.

Reactions of chlorine with cold and hot NaOH

(i) In cold (15°C) state, chlorine will react with NaOH to form hypochlorite and a halide.

$$2NaOH_{(aq)} + Cl_{2(g)} \xrightarrow{15°C} NaCl_{(aq)} + NaClO_{(aq)} + H_2O_{(aq)} \quad \ldots(a)$$

Sod. hypochlorite

The reaction is a disproportionation reaction, because the zero oxidation state of chlorine atom in Cl_2 is converted to –1 in chloride and +1 in hypochlorite.

(ii) Sodium hypochlorite which is produced in cold state in the above reaction decomposes forming sodium chloride andsodium chlorate at 70°C.

$$3NaClO_{(aq)} \longrightarrow 2NaCl_{(aq)} + NaClO_{3(aq)} \quad \ldots(b)$$

The reaction (b) involves the disproportionation of hypochlorite ion. To balance overall reaction in hot state, multiply equation (a) with 3 and then add (a) and (b).

$$6NaOH + 3Cl_2 \longrightarrow 3NaCl + 3NaClO + 3H_2O$$
$$3NaClO \longrightarrow 2NaCl + NaClO_3$$
$$6NaOH_{(aq)} + 3Cl_{2(g)} \longrightarrow 5NaCl_{(aq)} + NaClO_{3(aq)} + 3H_2O$$

The above two reactions (a) and (b) show that chlorine atoms are both reduced and oxidized.

Oxyacids of Halogens

The halogens containing acids of oxygen are called oxyacids.

- No oxygen containing stable acid of fluorine is known (HOF is prepared recently, but it is highly unstable).
- Other halogens (Cl, Br, I) form oxyacids which cannot be isolated in pure form and are stable only in aqueous solutions or in the form of their salts.

Q.6 Discuss the system of nomenclature used for oxyacids of halogen. Support your answer with examples.

Ans: **Nomenclature of oxyacids and their salts**

A system of nomenclature for these acids and their salts is based on the oxidation state of the halogen atom. According to this system, characteristic prefixes and suffixes are attached to a stem that is derived from the name of the central non-metal (halogen) atom. The system is as follows:

(i) An acid in which the oxidation state of parent atom (halogen) is +1 is called hypo----ous acid and its salt is called hypo----ite. e.g. HClO (Hypochlorous acid), NaClO (Sodium hypochlorite) etc.

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(ii) An acid in which the oxidation state of parent atom (halogen) is +3 is called -----ous acid and its salt is called ---- ite. e.g. $HClO_2$ (Chlorous acid), $NaClO_2$ (Sodium chlorite) etc.

(iii) An acid in which the oxidation state of parent atom (halogen) is +5 is called ----- ic acid and its salt is called ---- ate e.g. $HClO_3$ (Chloric acid), $NaClO_3$ (Sodium chlorate) etc.

(iv) An acid in which the oxidation state of parent atom is +7 is called per---- ic acid and its salt is called per---- ate. e.g. $HClO_4$ (Perchloric acid), $NaClO_4$ (Sodium perchlorate) etc.

(v) The root of the name of acid or salt indicates the parent name.

Oxyacids of Halogens

Oxidation state of halogen	Formula of the oxyacids of halogens			General names of	
	Chlorine	Bromine	Iodine	Oxyacids	Salts of oxyacids
+1	$HClO$	$HBrO$	HIO	Hypohalous acid	Hypo__ite
+3	$HClO_2$	------	------	Halous acid	__ite
+5	$HClO_3$	$HBrO_3$	HIO_3	Halic acid	__ate
+7	$HClO_4$		HIO_4, H_5IO_6	Perhalic acid	Per__ate

Properties of Oxyacids

(i) Acidic strength of oxyacids

The acidic strength increases with the increase in the number of oxygen atom. As the oxidation state of the halogen increases, the bonding electrons are shifted away from the H-atom and the tendency for the molecule to lose a proton increases. This accounts for the change of strength of oxyacids. The oxyacids of halogens show their strength in the order given below:

$$HXO_4 > HXO_3 > HXO_2 > HXO$$

(ii) Thermal stability

Thermal stability of oxyacids molecules increase by increasing the number of oxygen atoms. Perchloric acid $HClO_4$ is more stable than $HClO$ hypochlorous acid.

(iii) Oxidizing power of oxyacids

Oxidizing strength of oxyacids decreases by increasing oxidation number. $HClO$ and $HClO_2$ are good oxidizing agents. Oxidizing strength is given in the following order.

$$HClO > HClO_2 > HClO_3 > HClO_4$$

(iv) Polarity

In oxyacids the halogens serves as a central atom to which one or more oxygen atoms are covalently bonded. These bonds are polar in characters due to the electronegativity difference between halogen and oxygen.

(v) Relative strength of oxyacids of different halogens

The oxyacids of chlorine are stronger than the corresponding oxyacids of bromine which are, in turn, stronger than the corresponding oxyacids of iodine. It is due to decrease in the electronegativity and increase in the size of the halogen.

Perchloric Acid ($HClO_4$)

Preparation

Perchloric acid ($HClO_4$) is commonly obtained in aqueous solution. Pure anhydrous compound can be prepared by distilling a mixture of perchlorate ($KClO_4$) and conc. H_2SO_4 under reduced pressure.

$$KClO_{4(s)} + H_2SO_{4(conc.)} \xrightarrow[\text{Reduced pressure}]{\Delta} KHSO_{4(s)} + HClO_{4(\ell)}$$

Properties

1. Perchloric acid is a colourless, hygroscopic liquid.

2. At normal pressure, it freezes at –112°C and boils with decomposition at 90°C.
3. Perchloric acid is strongest of all the acids in an aqueous medium.

$$H_2O + HClO_4 \rightleftharpoons H_3O^+ + ClO_4^-$$

4. Pure perchloric acid decomposes explosively when heated. That is why it is stored and used as 67% solution in water.
5. Perchloric acid reacts with organic substances violently.

$HClO_4$ as an oxidizing agent

In the cold and dilute state perchloric acid is a very weak oxidizing agent but when hot and concentrated its oxidizing power is enhanced. Dissolving power of perchloric acid is enhanced due to its oxidizing strength. Due to its oxidizing effect, acidic strength and solubility of its salts, it is considered as a valuable analytical reagent.

Q.4 What is bleaching powder? How it is prepared commercially? Give its uses.

Bleaching Powder $Ca(OCl)Cl$

The chemical name of bleaching powder is calcium hypochlorite chloride. It is a yellowish white powder with strong smell of chlorine.

Preparation

Bleaching powder can be manufactured by the action of chlorine on dry slaked lime using any one of the following methods:

(a) Hasenclever's method (old method).

(b) Beckmann's method (modern method).

The reaction in both the cases will be:

$$\underset{\text{Slaked lime}}{Ca(OH)_2} + Cl_2 \longrightarrow \underset{\text{Bleaching powder}}{Ca(OCl)Cl} + H_2O$$

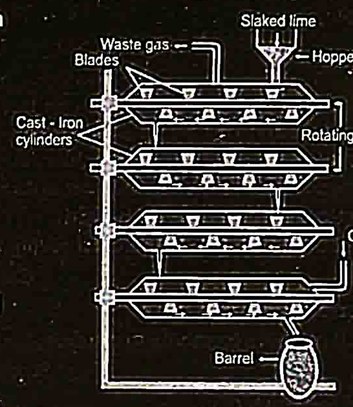
(a) Hasenclever's Method

- The apparatus used in this method consists of 4 to 8 iron cylinders placed one above the other horizontally.
- They are interconnected and provided with stirrers.
- The slaked lime is added in through a hopper in the upper cylinder and is transported from one cylinder to the other with rotating stirrers.
- Chlorine introduced into the lowest cylinder rises up and reacts with slaked lime to form beaching powder, which is collected through the outlet in the lowest cylinder.

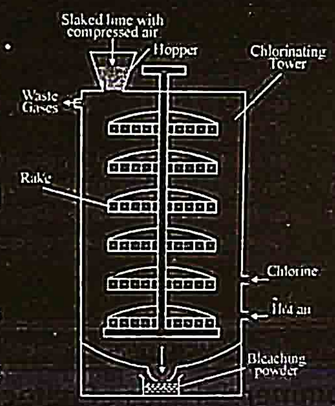
(b) Beckmann's Method

- In this method a cast iron tower with eight horizontal shelves is used.
- In each shelf there is a rotating rake.
- Powdered slaked lime is introduced through hopper at the top with compressed air.
- A mixture of hot air and chlorine are introduced from the base of the tower.
- The slaked lime is pushed down by the rotating rakes while chlorine rises up.
- Reaction between slaked lime and chlorine produces bleaching powder which is collected at the bottom of the tower.
- The apparatus works on the **counter-current principle** (in this principle reacting substances move in opposite directions and intermix together).
- Thus maximum reaction of slaked lime and chlorine is brought about with very little loss of chlorine.
- Bleaching powder should always be packed in air tight containers to avoid the loss of chlorine.

Blades + Stirrers is called rotating shaft.



Hasenclever's Method



Beckmann's Method

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Q. What is a counter – current principle?
Ans: The opposite flow of two adjacent fluids that can maximize the transfer rate is called counter – current principle.

Q.9 What happens when bleaching powder reacts with the following reagents dil. H_2SO_4, excess of conc. H_2SO_4, NH_3, HI and CO_2.

Chemical properties

1. As an oxidizing agent

It is an oxidizing agent. This property is due to the generation of hypochlorite ion (OCl^-) in water.

$$CaOCl_2 \rightleftharpoons^{H_2O} Ca^{+2} + Cl^- + ClO^-$$

2. Reaction with dilute acid

With dilute acid it gives hypochlorous acid.

$$2CaOCl_2 + \text{dil.}H_2SO_4 \longrightarrow CaSO_4 + CaCl_2 + 2HClO$$

Salts that contain more than one acid radical or basic radical are called as mixed salts.
Bleaching powder, $CaOCl_2$, is a mixed salt since though it contains only one cation (Ca^{2+}), it also contains two anions Cl^- and OCl^-.

3. Available chlorine

If excess of an acid (weak or strong) is added to bleaching powder, chlorine is given out.

$$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2 \uparrow$$
(excess)

The amount of chlorine thus set free is called **"available chlorine"**.

The activity of bleaching powder is measured in terms of available chlorine. The average percentage of available chlorine in bleaching powder is 35-40 percent. The bleaching action of bleaching powder is due to its oxidative character.

MCQ's
Which of the following is not a property of bleaching powder?
(a) Mixed salt
(b) Oxidizing agent
(c) Reducing agent
(d) Bleaching agent

4. Reaction with hydrogen halide

It oxidizes HCl, HBr and HI giving the corresponding halogens.

$$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$$

5. Reaction with ammonia

It oxidizes ammonia to nitrogen.

$$3CaOCl_2 + 2NH_3 \longrightarrow 3CaCl_2 + 3H_2O + N_2$$

6. Reaction with CO_2

Calcium hypochlorite reacts with carbon dioxide to form calcium carbonate and release chlorine.

$$CaOCl_2 + CO_2 \longrightarrow CaCO_3 + Cl_2$$

Uses

Bleaching powder is used:

(i) for the preparation of Cl_2 and O_2. It is also used in the manufacture of chloroform ($CHCl_3$).
(ii) as a disinfectant and for the sterilization of water.
(iii) for making unshrinkable wool.
(iii) to bleach cotton, linen and paper pulp. (Delicated fabrics like wool, silk etc. cannot be bleached with it because they could be damaged by chlorine).

MCQ's
Bleaching action of bleaching powder is due to
(a) Cl^- ion
(b) OCl^- ion
(c) Chlorate ion
(d) Perchlorate ion

Q.10 Discuss the various commercial uses of halogens and their compounds.

Commercial uses of halogens and their compounds

1. Fluorine and its compounds

Fluorine is used to prepare:

(i) **Freon** is the commercial name of low molecular mass fluorochlorocarbons, CCl_2F_2, $CClF_3$. These are being used as refrigerants and aerosol propellants.

(ii) **Teflon** $\{-CF_2-CF_2-\}_n$ which is a polymerized tetrafluoro ethylene compounds. It is a valuable plastic which resists the action of oxidants, acids and alkalies. It is used:
- to made corrosion-proof parts of machinery.
- for coating the electrical wiring.
- as a non-stick coating for cooking pans

(iii) **Halothane** which is used as an anesthetic.


Halothane

(iv) **Fluorides** which are used in toothpastes to build a protective coating on teeth.

2. Chlorine and its compounds

(i) Chlorine is used in the manufacture of:
- **bleaching powder.**
- antiseptics, insecticides, weed killers and herbicides.
- hydrochloric acid, which is the cheapest industrial acid.
- **polyvinyl chloride (PVC)** plastics.
- **chloroform** and **carbon tetrachloride** which are used as solvents.

(ii) Chlorine is used as a disinfectant in swimming pools and water treatment plants.

3. Bromine and its compounds

(i) Bromine is used in the preparation of:
- **ethylene dibromide ($C_2H_4Br_2$)** which is added to leaded gasoline to save the engine from lead oxide and lead sulphate deposits.
- **Silver bromide (AgBr)** which is used in Photography.

(ii) Bromine is also used as **fungicide.**

Tincture of iodine a disinfectant, is a solution usually contains 2–7% elemental iodine, along with potassium iodide or sodium iodide, dissolved in a mixture of ethanol and water.

4. Iodine and its compounds

The major applications of iodine are in pharmaceutical industry.

(i) It is used as disinfectant and germicide.
(ii) Tincture of iodine and iodex are popular preparations of iodine.
(iii) Diet with insufficient iodide ions leads to an enlargement of the thyroid (Goiter). To ensure the presence of iodide ion in the diet, sodium or potassium iodide is added to the common salt which is known as iodized salt.

Q.13 (i) What is Iodized salt?

Ans **Iodized salt:**
"When common salt (NaCl) contains 0.02% KI by weight, it is called iodized salt".
- Sodium iodide can also be used in common salt to get iodized salt.
- Diet with insufficient iodide ions leads to an enlargement of **"thyroid" (Goiter).**
- To ensure the presence of iodide ions in the diet, iodized table salt is used to prevent goiter.

Q.13 (ii) What are Freons and Teflon?

Ans **Freon:**
"Freon is the commercial name of low molecular mass Fluorochlorocarbons."


Dichlorodifluoromethane

Chlorotrifluoromethane

Uses:
Freons are being used as refrigerants and aerosol propellants.

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Teflon:
"It is a polymerized tetra-fluoroethylene compound".
Fluorine is used to prepare Teflon.



Teflon

Uses:

(i) It is a valuable plastic which resists the action of oxidants, acids and alkalies.
(ii) Corrosion proof parts of machinery are made of it.
(iii) It is used for coating the electrical wiring.
(iv) It is used as a non-stick coating for cooking pans.

Q.13 (vi) Which halogen is used as an antiseptic?

Ans Both chlorine and bromine are used as antiseptic.

Q.13 (vii) Which halogen is used in water treatment to kill bacteria?

Ans Chlorine.

Noble Gases

Introduction

- The elements helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn) are placed in the zero group or group VIIIA of the periodic table.
- All the elements of this group are colourless and odourless monoatomic gases which can be liquefied and solidified. These are called noble gases or sometime known as rare gases.

Electronic Configurations and Physical Properties of Noble Gases

Property	He	Ne	Ar	Kr	Xe	Rn
Atomic number	2	10	18	36	54	86
Electronic configurations	$1s^2$	$[He]2s^2 2p^6$	$[Ne]3s^2 3p^6$	$[Ar]3d^{10} 4s^2 4p^6$	$[Kr]4d^{10} 5s^2 5p^6$	$[Xe]5d^{10} 6s^2 6p^6$
Ionization energy ($kJmol^{-1}$)	2372	2081	1521	1351	1170	1037
Atomic radius (pm)	40	70	94	109	130	140
Melting points (°C)	-272	-249	-189	-157	-112	-71
Boiling points (°C)	-269	-246	-186	-153	-108	-61
Water solubility (ml/lit) at 20°C	13.8	14.7	37.9	73.00	110.9	---
Heat of vapourization ($kJmol^{-1}$)	0.08	1.77	6.5	9.7	13.7	18.0

Occurrence

The noble gases occur as minor constituents of the atmosphere (about 1%). The noble gases are isolated from air, either by fractional distillation or by some chemical method. The principal commercial source of Ne, Ar, Kr and Xe is air.

Helium: It is present on earth as a result of radioactive decay. After hydrogen, it is the second most abundant element in the universe. α- particles are doubly ionized helium atoms He^{2+}. It is simple and economical to isotale the helium gas from certain natural gases by liquefaction method.

Neon: It is $1/65000^{th}$ part of the atmosphere and it is also isolated during liquefaction of air. In a discharge tube, neon glows reddish (of all the noble gases, the discharge of neon is the most intense at ordinary voltage and current). Liquid neon has over 40 times more refrigeration capacity than liquid helium.

Argon: It is a colourless and odourless gas. It is very inert and not known to form any true chemical compounds. It is obtained as a by-product during the liquefaction of air.

Krypton: Traces of krypton are present in air. It is a colourless, odourless and fairly expensive gas. It is characterized by its brilliant green and orange spectral lines. Its compound, krypton difluoride (KrF_2) can be prepared by various methods.

Xenon: It is present in the atmosphere to a very small extent (0.08 ppm). It is obtained as a by-product during the fractional liquefaction of air. Xenon is available commercially in cylinders at high pressure. It reacts with fluorine but not with water. However it is slightly soluble in water to the extent of about 110 ml/lit at 20°C.

Radon: It is the α-decay product of the radium. Radon is present to a very small extent in the atmosphere and it could be obtained as a by-product from the liquefaction of air. However, the small quantities of this gas which are usually needed can be collected from the radioactive decay of radium isotopes.

$$^{226}Ra \longrightarrow {}^{222}Rn + {}^{4}He$$

Physical properties

(i) The noble gases have valence shells which are closed octets (except He). Due to closed shells their ionization energy values are very high.
(ii) They have low boiling points. The boiling point of helium is the lowest of any known substance. Their boiling points increase with increasing atomic number down the group.
(iii) The very low values of melting and boiling points and low heats of vaporization show that noble gases have weak forces of attraction between their atoms. As there are no ordinary electron pair interactions, these weak forces must be of the van der Waals type.
(iv) The solubility of the noble gases in water increases with increasing atomic number. This is because the bigger atoms are more readily polarized by water molecules.

Q.11 What are noble gases? Explain their inertness on the basis of their electronic configuration.

Ans The elements helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn) are placed in the zero group or group VIIIA of the periodic table. All the elements of this group are colourless and odourless monoatomic gases which can be liquefied and solidified. These are called noble gases or sometime known as rare gases. The noble gases have valence shells which are closed octets (except He). Due to closed shells their ionization energy values are very high. That's why noble gases are inert.

Compounds of Xenon

Xenon reacts directly with fluorine only. The known oxidation state of Xe in its compounds range from +2 to +8. These compounds are stable and can be obtained in large quantities. Some important compounds of Xe are as follows:

Compounds of Xenon

Oxidation state of xenon	Compound	Physical form	Melting point (°C)
+2	XeF_2	Colourless crystals	140
+4	XeF_4	Colourless crystals	114
+4	$XeOF_2$	Colourless crystals	90
+6	XeF_6	Colourless crystals	48
+6	$XeOF_4$	Colourless liquid	-28
+6	XeO_3	Colourless crystals	25 (Explodes)
+8	XeO_4	Colourless gas	-39.9 (Explodes on warming)

(A) Fluorides of Xenon

Three known fluorides of Xenon are:

(i) XeF_2 (Xenon difluoride)

Preparation

It can be prepared by direct interaction of the elements. The compounds formed should be removed immediately from the reaction zone, otherwise further reaction with F_2 will give XeF_4.

The reaction is completed in about 8 hours.

$$Xe + F_2 \longrightarrow XeF_2$$

Properties

- XeF_2 is a crystalline solid.
- It is stored in nickel vessels.
- XeF_2 is a mild fluorinating agent.

(ii) XeF_4 (Xenon tetrafluoride)

Preparation

It can be prepared by heating a mixture of Xe and F_2 in 1:5 ratio in a nickel container under 6 atmospheric pressure for a few hours. It can be stored in nickel vessels.

$$Xe + F_2 \longrightarrow XeF_2$$
$$XeF_2 + F_2 \longrightarrow XeF_4$$

Properties

Its properties are similar to that XeF_2 but it is a strong fluorinating agent.

(iii) XeF_6 (Xenon hexafluoride)

Preparation

It requires more severe conditions. Xe and F_2 are taken in 3:20 ratio in a stainless steel vessel and heated to 300°C at 50 atmospheric pressure. More than 95% conversion to XeF_6 takes place.

$$Xe + F_2 \longrightarrow XeF_2$$
$$XeF_2 + F_2 \longrightarrow XeF_4$$
$$XeF_4 + F_2 \longrightarrow XeF_6$$

Properties

- XeF_6 is a crystalline solid.
- It is coloulress in the solid state but yellow in liquid and gaseous forms.

Chemical Reactions of Fluorides of Xenon

(i) Fluorides of xenon can be reduced with hydrogen at 400°C, giving xenon and hydrofluoric acid.

$$XeF_2 + H_2 \longrightarrow Xe + 2HF$$
$$XeF_4 + 2H_2 \longrightarrow Xe + 4HF$$
$$XeF_6 + 3H_2 \longrightarrow Xe + 6HF$$

(ii) Xenon tetra-fluoride is a good fluorinating agent and can be used to prepare metal fluorides as follows.

$$XeF_4 + 2Hg \longrightarrow Xe + 2HgF_2$$

(iii) Reaction occurs with explosion when XeF_4 is brought in contact with liquid ammonia.

$$3XeF_4 + 4NH_3 \longrightarrow 3Xe + 12HF + 2N_2$$

(iv) Hydrolysis of XeF_6 with small amount of water gives $XeOF_4$.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

Q.12 Write notes on the followings.
(i) Oxyfluorides of xenon.

Xenon Oxyfluorides

Preparation

Xenon oxytetrafluoride, $XeOF_4$ is formed by a rapid reaction of XeF_6 with silica (quartz).

$$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$$

Properties

- $XeOF_4$ is a colourless volatile liquid.
- It can be kept in nickel vessel.

- It reacts with water to give XeO_3.

$$XeOF_4 + 2H_2O \longrightarrow XeO_3 + 4HF$$

Xenon oxydifluoride ($XeOF_2$)

- Xenon oxydifluoride ($XeOF_2$) is obtained when xenon reacts with oxygen difluoride in an electric discharge.

$$Xe + F_2O \longrightarrow XeOF_2$$

Oxides of Xenon

There are two oxides of xenon:

(i) Xenon trioxide.
(ii) Xenon tetraoxide.

1. Xenon Trioxide (XeO_3)

Preparation

Xenon trioxide can be obtained when XeF_6 is hydrolysed slowly.

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

Properties

- It is a crystalline solid.
- It explodes at very low temperature.
- It is weakly acidic and its aqueous solution is almost non conductor.

2. Xenon Tetraoxide (XeO_4)

It is obtained by the addition of barium or sodium perxenate to conc. H_2SO_4.

$$Ba_2XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2BaSO_4 + 2H_2O$$
$$Na_4XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2Na_2SO_4 + 2H_2O$$

Q.12 (ii) Write down the applications of noble gases.

Applications of the Nobel Gases

Helium

- It is used in weather balloons, in welding and in traffic signal light.
- A mixture of 80% helium and 20% oxygen is used for breathing by the sea divers.
- It is used as a cooling medium for nuclear reactors.

Neon

- It is largely used in making neon advertising signs, in high voltage indicators and TV tubes.
- Neon and helium arc is used in making glass lasers.

Argon

- It is used in electric light bulbs, in fluorescent tubes, in radio tubes and in Geiger counters (used to detect radioactivity).
- It is also used for arc welding and cutting.

Krypton

It is used to fill fluorescent tubes and in flash lamps for high speed photography.

Xenon

It is used in bactericidal lamps.

Radon

Radon being radioactive is used in radiotherapy for cancer, and for earth quake prediction.

Q.13 (viii) Name the gas, which is used for earthquake prediction.

Ans Among noble gases, radon (Rn) being radioactive is used for earthquake prediction.

Q.13 (ix) Name the gas, which is used in bactericidal lamps.

Ans Xenon (Xe) is used in bactericidal lamps.

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Q8. In the following sets, arrange the substances in order of the property indicated. Give reasons.

(a) Increasing acidic character
$HClO$, $HClO_2$, $HClO_3$, $HClO_4$

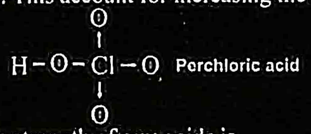
(b) Increasing oxidizing power
F_2, Cl_2, Br_2, I_2

Ans **Arrange and give reasons:**

(a) Increasing acidic character

Reason:

The strength of oxy acids of Halogens increases with increase in Number of oxygen atoms. As the oxidation state of halogen atom in oxyacids increases, the bonding electrons are shifted away from hydrogen atom and tendency of molecules to lose proton increases. This account for increasing the strength of oxy-acids.



Perchloric acid

Thus increasing order of acidic strength of oxy-acids is
$HClO < HClO_2 < HClO_3 < HClO_4$

(b) Increasing oxidizing power

Reason:

The oxidizing power of halogens depends upon following factors:

(i) Energy of dissociation
(ii) Electron affinity of atoms
(iii) Hydration Energy of ions
(iv) Heat of vapourization (for Br_2 and I_2)

If halogen has low energy of dissociation, a high electron affinity and a higher hydration energy of its ions, it will have high oxidizing power.

Thus, the order of increasing oxidizing power of halogens is

$$I_2 < Br_2 < Cl_2 < F_2$$

KEY POINTS

1. The halogens are very **reactive**. Intermolecular forces in halogens increase down the group, fluorine is a gas but iodine is solid.
2. They form ionic compounds with s-blocks metals, covalent compounds with p-block elements and complex ions with d-blocks metals. Fluorides are usually **ionic**.
3. They show oxidation state $-1, +1, +3, +5, +7$ but fluorine shows the oxidation state of -1 only.
4. Oxidizing power of halogens **decreases** down the group in the following order
$$F_2 > Cl_2 > Br_2 > I_2$$
5. Reducing power of halide ions decreases from I^- to Br^-. Chloride and fluoride ions are not reductants.
6. Chlorine, bromine and iodine form their respective oxides and oxyacids.
7. Halogens and their compounds are used for bleaching, refrigeration and as aerosols, etc.
8. Noble gases are placed in **zero (VIII-A)** group of periodic table.
9. They have valence shells which are closed octets (except helium).
10. Very low values of melting and boiling points show that there have very weak forces of attraction between their atoms.
11. Oxides, fluorides and oxyfluorides of xenon can be prepared.
12. Noble gases have multidimensional uses.

SOLVED OBJECTIVE EXERCISE

Q1. Fill in the blanks.

(i) The halogen with the highest electronegativity is ____
(ii) HI is _____ agent.
(iii) The only halogen acid which is not a strong acid is _____

(iv) Tincture of _____ is a common antiseptic.
(v) The halogen with the lowest melting and boiling points is _____.
(vi) Bleaching powder is prepared from _____ and _____.
(vii) _____ is the halogen which causes burns on the skin which heal slowly.
(viii) _____ is the used for making unshrinkable wool.
(ix) A mixture of _____ and _____ is used for breathing by the sea divers.
(x) Noble gas used to fill fluorescent tubes is _____.

Answer Key.

(i)	Fluorine	(ii)	Reducing	(iii)	HF	(iv)	Iodine
(v)	Fluorine (F_2)	(vi)	$Ca(OH)_2$, Cl_2	(vii)	Bromine	(viii)	Bleaching powder
(ix)	80% He and 20% O_2	(x)	Krypton and Argon				

Q2. Indicate True or false.

(i) HF is used for etching glass.
(ii) HI is weaker reducing agent as compared to HF.
(iii) Bleaching powder is completely soluble in water.
(iv) The formula of perchloric acid is $HClO_3$.
(v) On warming, aqueous KOCl disproportionates as follows.
$$3KOCl \rightarrow 2KCl + KClO_3$$
(vi) α-particles emitted by radioactive elements are ions of radon.
(vii) Radon is the only one of the noble gases that is radioactive.
(viii) The molecules of the noble gases are all monoatomic
(ix) Argon is used to fill electric bulbs.
(x) The noble gas which is present in the largest amount in atmosphere is krypton.

Answer Key.

(i)	True	(ii)	False	(iii)	True	(iv)	False	(v)	True
(vi)	False	(vii)	True	(viii)	True	(ix)	True	(x)	False

Q3. Multiple Choice Questions. Encircle the correct answer.

(i) Which of the following hydrogen halide is the weakest acid in solution?
(a) HF (b) HBr (c) HI (d) HCl

(ii) Chlorine heptaoxide (Cl_2O_7) reacts with water to form.
(a) Hypochlorous acid (b) Chloric acid
(c) Perchloric acid (d) Chlorine and oxygen

(iii) Hydrogen bond is the strongest between the molecules of:
(a) HF (b) HCl (c) HBr (d) HI

(iv) Which halogen will react spontaneously with $Au_{(s)}$ to produce Au^{3+}?
(a) Br_2 (b) F_2 (c) I_2 (d) Cl_2

(v) The anhydride of $HClO_4$ is:
(a) ClO_3 (b) ClO_2 (c) Cl_2O_5 (d) Cl_2O_7

(vi) Bleaching powder may be produced by passing chlorine over:
(a) calcium carbonate (b) hydrated calcium sulphate
(c) anhydrous calcium sulphate (d) calcium hydroxide
(e) magnesium hydroxide

(vii) Which halogen occurs naturally in a positive oxidation state?
(a) Fluorine (b) Chlorine (c) Bromine (d) Iodine

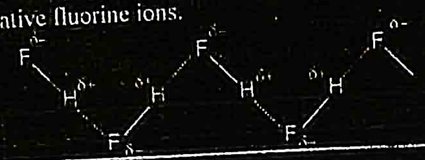
(viii) Which is the strongest acid?
(a) HClO (b) $HClO_2$ (c) $HClO_3$ (d) $HClO_4$

(ix) An element that has a high ionization energy and tends to be chemically inactive would most likely to be:
(a) an alkali metal (b) a transition element (c) a noble gas (d) a halogen

(x) Which of the following represents the correct electronic configuration of the outermost energy level of an element of zero (VIIIA) group in the ground state.
(a) s^2p^3 (b) s^2p^4 (c) s^2p^5 (d) s^2p^6

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Solved Exercise MCQs

Q. No	Answer	Reason
(i)	(a) HF	HF is weakest acid because partially positive hydrogen ion is entrapped b/w highly electronegative fluorine ions. 
(ii)	(e) Perchloric acid	$Cl_2O_7 + H_2O \longrightarrow 2HClO_4$ Cl_2O_7 is anhydride of perchloric acid.
(iii)	(a) HF	Electronegativity difference between H(2.1) and F(4.0) is 1.9 which is maximum so H-bond is formed which is strongest.
(iv)	(d) Cl_2	Cl_2 reacts spontaneously with $Au_{(s)}$ to form Au^{+3}, so gold becomes dissolved due to formation of soluble chloride. This process is used in aqua regia.
(v)	(d) Cl_2O_7	$2HClO_4 \xrightarrow{-H_2O} Cl_2O_7$
(vi)	(d) Calcium hydroxide	$Ca(OH)_2 + Cl_2 \longrightarrow Ca(OCl)Cl + H_2O$ Bleaching Powder
(vii)	(d) Iodine	In $NaIO_3$, oxidation state of 'I' is +5 & in $NaIO_4$, oxidation state is +7. Other halogens may have positive oxidation states but in artificial compounds.
(viii)	(d) $HClO_4$	$HClO_4$ is strongest acid because oxidation state of halogen increases and binding electrons are shifted away from hydrogen, and hydrogen is released comparatively easily.
(ix)	(c) A noble Gas	Noble Gas has complete valence shell so it tends to be inactive.
(x)	(d) s^2p^6	VIII A group elements have eight electrons in their valence shell so their valence shell electronic configuration is s^2p^6.

Previous Board Questions

1. What are Freons and Teflon?
2. Give reaction of bleaching powder with:
   (a) Excess of H_2SO_4 (b) NH_3
3. Write four applications of noble gases.
4. The acidic strength of the oxyacids of halogens increases with the increase in the number of oxygen atoms why?
5. Why HF is a weaker acid than HCl.
6. Why fluorine and chorine act as decolorizing agents?
7. How are the halogen acids ionized in water? Also give the chemical equation.
8. What do you mean by available chlorine and how is it calculated?
9. Why iodine has metallic luster?
10. What are Noble Gases and why are they inert?
11. Why $HClO_4$ is a stronger acid than $HBrO_4$ than HIO_4?
12. Why the oxidation state of noble gases is usually zero?
13. What is iodized salt?
14. Which halogen is used as an antiseptic and which one has violet fumes?
15. Why iodine has metallic shine?
16. How does bleaching powder act as bleaching agent for fabrics?
17. What is meant by "Disproportionation reaction"? Give an example of it?

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CHAPTER 6

TRANSITION ELEMENTS

Transition Elements

"Those elements which have partially filled d or f – subshells in atomic state or in any of their commonly occurring oxidation states are called transition elements".

The d-block and the f-block elements are called transition elements because they are located between the s and p-block elements and their properties are in transition between the metallic elements of the s-block and nonmetallic elements of the p-block.

Q. Why d and f-Block elements are called transition elements?

Transition elements are divided into two types.

1. d-Block Elements

The elements having partially filled d-subshell are called d-block elements. Zinc, cadmium and mercury are also included in transition elements although they have no partially filled d-orbital. Copper in zero state has no d-subshell partially filled but Cu^+ has configuration [Ar] $3s^2$, $3p^6$, $3d^9$ and transitional in character. Ag and Au also have no partially filled d-orbital in zero oxidation state. But Ag^{+2} has $4d^9$ and Au^{+3} has $5d^8$ electronic configuration. d-block elements are also called outer **transition elements.**

2. f-Block Elements

"The elements having f-subshell partially filled in their common oxidation state are called f-block elements. f-block elements are also called inner transition elements".

f-block transition elements include two rows at the bottom of periodic table. First row is called **Lanthanides** while second row is called **Actinides**. All actinides are radioactive in nature.

Electronic configurations of three series of d-block elements

3d-block elements		4d-block elements		5d-block elements	
Elements	Electronic configuration	Elements	Electronic configuration	Elements	Electronic configuration
Sc (21)	$[Ar]3d^14s^2$	Y (39)	$[Kr]4d^15s^2$	La (57)	$[Xe]5d^16s^2$
Ti (22)	$[Ar]3d^24s^2$	Zr (40)	$[Kr]4d^25s^2$	Hf (72)	$[Xe]4f^{14}5d^26s^2$
V (23)	$[Ar]3d^34s^2$	Nb (41)	$[Kr]4d^45s^1$	Ta (73)	$[Xe]4f^{14}5d^36s^2$
Cr (24)	$[Ar]3d^54s^1$	Mo (42)	$[Kr]4d^55s^1$	W (74)	$[Xe]4f^{14}5d^46s^2$
Mn (25)	$[Ar]3d^54s^2$	Te (43)	$[Kr]4d^55s^2$	Re (75)	$[Xe]4f^{14}5d^56s^2$
Fe (26)	$[Ar]3d^64s^2$	Ru (44)	$[Kr]4d^75s$	Os (76)	$[Xe]4f^{14}5d^66s^2$
Co (27)	$[Ar]3d^74s^2$	Rh (45)	$[Kr]4d^85s^1$	Ir (77)	$[Xe]4f^{14}5d^76s^2$
Ni (28)	$[Ar]3d^84s^2$	Pd (46)	$[Kr]4d^{10}$	Pt (78)	$[Xe]4f^{14}5d^96s$
Cu (29)	$[Ar]3d^{10}4s^1$	Ag (47)	$[Kr]4d^{10}5s^1$	Au (79)	$[Xe]4f^{14}5d^{10}6s$
Zn (30)	$[Ar]3d^{10}4s^2$	Cd (48)	$[Kr]4d^{10}5s^2$	Hg (80)	$[Xe]4f^{14}5d^{10}6s^2$

The detailed electronic configuration of first series of d-block elements is given blow.

		3d$_{xy}$	3d$_{yz}$	3d$_{xz}$	3d$_{x^2-y^2}$	3d$_{z^2}$	4s
Sc	[Ar]	↑					↑↓
Ti	[Ar]	↑	↑				↑↓
V	[Ar]	↑	↑	↑			↑↓
Cr	[Ar]	↑	↑	↑	↑	↑	↑
Mn	[Ar]	↑	↑	↑	↑	↑	↑↓
Fe	[Ar]	↑↓	↑	↑	↑	↑	↑↓
Co	[Ar]	↑↓	↑↓	↑	↑	↑	↑↓
Ni	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓
Cu	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Zn	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

In this electronic configuration chromium and copper disobey the n + l rule. In case of chromium one electron from s-sub shell have been used the half-fill d-subshell to complete it. This is because half filled d-subshell (d^5) and full filled (d^{10}) d-subshell are most stable.

Main Group Elements And Transition Elements

Group	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	H																	He
2	Li	Be	Transition Elements										B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca											Ga	Ge	As	Se	Br	Kr
5	Rb	Sr											In	Sn	Sb	Te	I	Xe
6	Cs	Ba											Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac	104	105	106	107											

Q. What are non-typical transition elements? In which respect they differ from those of typical transition elements?

Ans

Non-typical transition elements

The elements (Zn, Cd, Hg) of group IIB and (Sc, Y, La) of group IIIB are called non-typical transition elements.

Group IIB Elements

According to definition of transition elements, Zn, Cd and Hg should not be placed with d-block elements because they do not have a partially filled d-orbital either as elements or in any of their oxidation state.

Group IIIB elements

They have one electron in the d-sub-shell of their atoms. But in compounds, they mostly occur as the tripositive ions (Sc^{+3}, Y^{+3}, La^{+3}), having no d-electron. In this way they exhibit the properties of main group elements.

Properties differing from typical transition elements

(i) These elements (Zn, Cd, Hg) are diamagnetic.

(ii) They do not show variable oxidation state.

(iii) Most of their compounds are colourless.

Common properties of Transition elements:

i) Partially filled d & f orbitals
ii) Coloured compounds formation
iii) Paramagnetic behaviour
iv) Variable oxidation states
v) Catalytic properties
vi) Complex compound formation

Properties of Transition Elements

Because of a similar electronic configuration, the d-block elements closely resemble one another in their physical and chemical properties. Some of the points of their resemblance are given below.

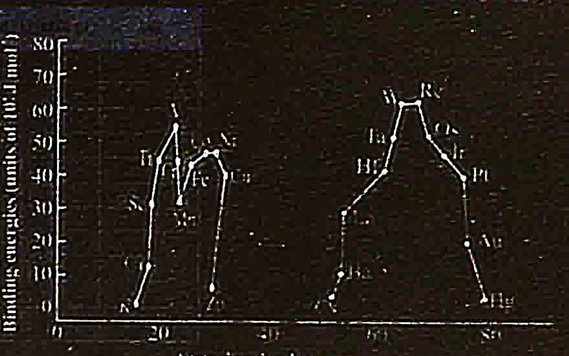
1. They are all metals in true sense, some of which play important role in industry. Ti, Fe, Cr, Ni, Cu, Mo, W, Zr, Nb, Ta, Th, etc.
2. They are all hard and strong metals with high melting and boiling points. They are also good conductors of heat and electricity.
3. They form alloys with one another and also with other elements.
4. With few exceptions, they show variable valency or oxidation state.
5. Their ions and compounds are coloured in solid state as well as in solution forms, at least in one, if not all the oxidation states.

Q.4 How does the electronic configuration of valence shell affect the following properties of the transition elements?

General Characteristics of Transition Elements

(a) Binding energies

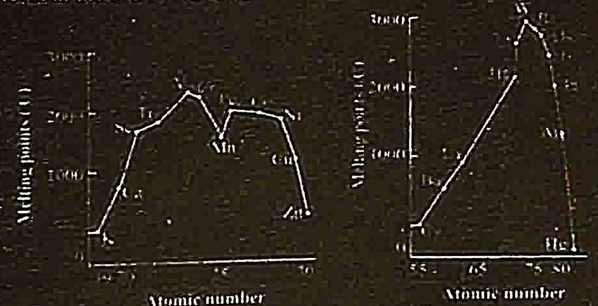
- Transition metals show good mechanical properties. They are tough, malleable and ductile. The toughness of these metals indicates strong metallic binding. This is because, apart from s-electrons of the outer most shell, the electrons of underlying half-filled d-orbitals also participate in binding.
- In moving from left to right in any transition series, the number of unpaired electrons increases up to group VB and VIB, after that pairing takes place and number of unpaired electrons goes on decreasing until it becomes zero at group IIB.
- Therefore binding is stronger up to group VIB and weakens progressively up to group IIB. This trend of variation in binding energies is shown in figure. In the first transition series, the general increase in binding energy ends at vanadium. This is due to the change in metallic structure. Manganese has somewhat low binding energy. In the third transition series, the increase in binding energy ends at tungsten when all the 5d electrons contribute to binding.



Binding energies of the elements of the first and third transition series

(b) Melting points and boiling points

Transition metals have very high melting and boiling points due to strong binding forces present between their atoms. Melting points increase up to the middle of the series and then decrease to a minimum level at the end of the series.



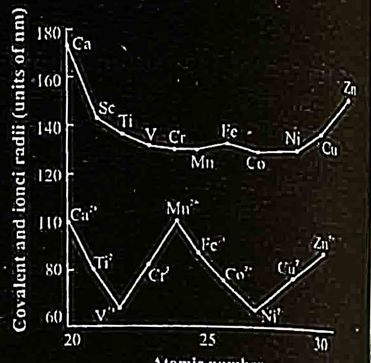
Melting points of the elements of the first and the third transition series

Melting points and boiling points of elements is directly related with the strength of binding forces. Greater is strength of bond, greater will be melting and boiling points.

(c) Covalent Radii and Ionic Radii

The covalent radii decrease rapidly at the start of the series, then become almost constant, and finally begin to increase at the end of the series. The increase in covalent radii is possibly due to the fact that the filled 3d orbital have contracted into the electron core and so shield the outer 4s electrons more effectively form the nucleus.

Changes in the ionic radii along the series are much less regular, so that periodic trends in the properties of these ions are difficult to rationalize.



Covalent radii and ionic radii (for M^{2+}) of first transition series elements

(d) Paramagnetism

Paramagnetic substances: Substances which are weakly attracted by a strong magnetic field are called Paramagnetic substances. e.g. $MnSO_4, FeCl_2, NiCl_2$ etc.

Diamagnetic substances: Those substances which are weakly repelled by a strong magnetic field are called diamagnetic substances. e.g. $ZnCl_2$, $ScCl_3$, CuCl etc.

Reason of Paramagnetism

Paramagnetic behaviour is caused by the presence of unpaired electrons in an atom, molecule or ion because there is a magnetic moment associated with the spinning electron. It increases with increase in the number of unpaired electrons. When the electrons are paired in an orbital, then magnetic moments are cancelled out and the substances become diamagnetic.

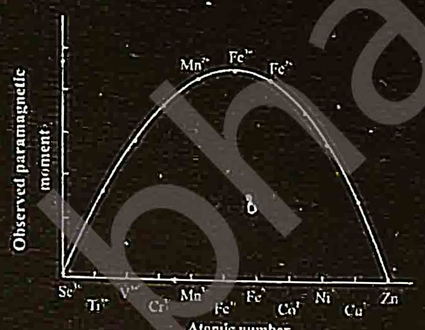
Ion	3d orbital electronic structure	No. of unpaired electrons
Sc^{3+}		0
Ti^{3+}	↑	1
V^{3+}	↑ ↑	2
Cr^{3+}	↑ ↑ ↑	3
Mn^{3+}	↑ ↑ ↑ ↑	4
Mn^{2+}, Fe^{3+}	↑ ↑ ↑ ↑ ↑	5
Fe^{2+}	↓↑ ↑ ↑ ↑	4
Co^{2+}	↓↑ ↓↑ ↑	3
Ni^{2+}	↓↑ ↓↑ ↓↑	2
Cu^{2+}	↓↑ ↓↑ ↓↑ ↑	1
Zn^{2+}	↓↑ ↓↑ ↓↑ ↓↑	0

Periodic trend

The paramagnetic behaviour is the strongest for Fe^{3+} and Mn^{2+} and decreases on both sides of the first transition series. The reason is that both Mn^{+2} and Fe^{+3} have 5 unpaired electrons each. The number of unpaired electrons decreases gradually to zero on both sides as it is clear from above table.

The following figure shows the variation in the paramagnetic effect of the ions belonging to the first transition series.

Q. Why Mn^{2+} & Fe^{3+} have strong magnetic properties?



Variation in the paramagnetic effect shown by the selected ions across the first transition series

Bohr magneton (B.M) is a unit of magnetic moment used to describe atomic, molecular, or nuclear magnets.

$$1 B.M = \frac{eh}{4\pi mc}$$

Gouy balance is used to determine the magnitude of paramagnetic nature and number of unpaired electrons of an atom.

(e) Oxidation state

One of the most important properties of transition elements is that they exhibit variable oxidation states. They show variable valencies because of the involvement of the unpaired d-electrons in addition to s-electrons in bond formation. All 3d series elements show an oxidation state of +2 in addition to higher oxidation states.

Commonly Occurring Oxidation States of the 1st Series of Transition Elements

		Oxidation states
Sc	$[Ar]3d^1 4s^2$	2 3
Ti	$[Ar]3d^2 4s^2$	2 3 4
V	$[Ar]3d^3 4s^2$	2 3 4 5
Cr	$[Ar]3d^5 4s^1$	2 3 4 5 6
Mn	$[Ar]3d^5 4s^2$	1 2 3 4 5 6 7
Fe	$[Ar]3d^6 4s^2$	1 2 3 4 5 6
Co	$[Ar]3d^7 4s^2$	2 3 4 5
Ni	$[Ar]3d^8 4s^2$	2 3 4
Cu	$[Ar]3d^{10} 4s^1$	1 2 3
Zn	$[Ar]3d^{10} 4s^2$	2

Highest oxidation state is shown by Ruthenium & Osmium which is +8.

MCQ's

Which of the following is most stable oxidation state of Mn?

(a) Mn^{+2} (b) Mn^{+3}
(c) Mn^{+4} (d) Mn^{+5}

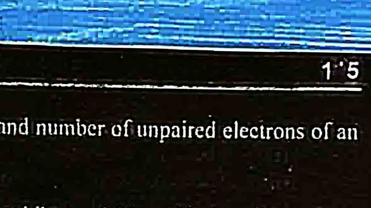
HINT:

d^0, d^5 & d^{10} are stable electronic configuration

+2 oxidation state is shown when only the 2s electrons are involved in bonding. In the highest oxidation states of the first five elements, all the s and d electrons are used for bonding. Manganese has highest oxidation (+7) among the first transition series. After Mn, the number of oxidation states decreases as the d subshell fills up and fewer unpaired electrons are available for bond formation.

(f) Colour

In transition elements, the d orbitals are responsible for the colour development in their compounds. When these orbitals are involved in bonding, they split up into two energy levels, one set has a higher energy than the other. The electrons residing in low energy d-orbitals absorb a part of the visible light and jump to high energy d orbitals. The process is called d-d transition. The energy difference of d-orbitals varies from ion to ion.

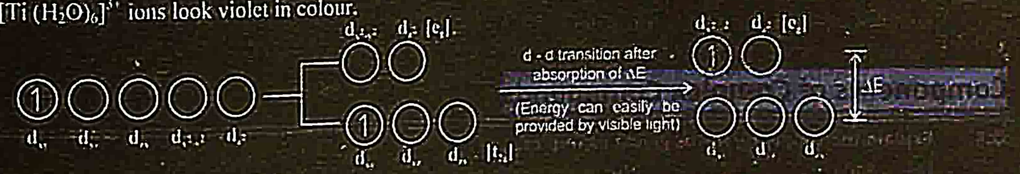


Complimentary colours

Thus, every ion absorbs a different wavelength and transmits the remaining set of wavelengths that gives different colours to the ions.

Example

In $[Ti(H_2O)_6]^{3+}$ ion, yellow light is absorbed while most of the blue and red lights are transmitted. Therefore, the solution of $[Ti(H_2O)_6]^{3+}$ ions look violet in colour.



Absorption of yellow light by $[Ti(H_2O)_6]^{3+}$

Q. What are interstitial compounds? Write down their different characteristics.

Ans

Interstitial compounds

When small non-metal atoms like H, B, N, C enter the interstices of transition metals and impart useful features to them, they are called interstitial compounds.

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Examples: TiC, Mn_4N, TiH, Fe,H etc.

(i) These are non-stoichiometric compounds.
(ii) They are neither typically ionic nor covalent.
(iii) They have some properties different from those of transition metals, e.g. hardness, melting points, chemical properties etc.

(h) Alloy formation (Substitutional compounds)

"A solid solution of metals is called alloy". Due to the similarity in their sizes, some transition metal atoms are able to replace one another in the metallic lattice and form substitutional alloys among themselves. Alloy steel is an important example of this type of material in which iron atoms are substituted by chromium, manganese and nickel atoms, etc. to give the steel more useful properties. Other examples are brass, bronze, coinage alloys, etc.

Alloy	Composition
Brass	Cu 60 - 80%, Zn 40 - 20%
Bronze	Cu 75 - 90%, Sn 25 - 10%
German silver	Cu 56 %, Zn 24%, Ni 20%
Gun metal	Cu 87 %, Zn 3%, Sn 10%

Complex compounds

"A substance formed when one or more anions or neutral molecules are bonded with a metal atom or ion is called complex".

or

"The compounds containing the complex molecules or complex ions and capable of independent existence are called coordination compounds or complexes."

In complex, coordinate covalent bond is present so it is called coordination compounds.

Example: When the aqueous solutions of $Fe(CN)_2$ and KCN are mixed together and evaporated, a new compound is obtained which in aqueous solution does not ionize as Fe^{++} and CN^- ions but ionizes as K^+ ion and $[Fe(CN)_6]^{4-}$ ion (Ferrocyanide ion). On this basis it has been given a formula $K_4[Fe(CN)_6]$.

$$Fe(CN)_2 + 4KCN \longrightarrow K_4[Fe(CN)_6] \xrightarrow{\text{Ionization}} 4K^+ + [Fe(CN)_6]^{4-}$$

Here $[Fe(CN)_6]^{4-}$ is called a complex ion.

There are three types of complexes.

1. A complex containing a simple cation and complex anion e.g: $K_4[Fe(CN)_6]$
2. A complex cation and simple anion, e. g: $[Cu(NH_3)_4]SO_4$.
3. A netural complex, e.g. $[Ni(CO)_4]$

Components of Complex Compounds

Q.5 Explain the following terms giving examples.
(a) Ligands (b) Coordination sphere (c) Coordination number
(d) Central metal atom (e) Chelates

Ans

(a) Ligands

"The atoms, ions or neutral molecules, which surrounds the central metal ion and donate electron pairs to it are called ligands".

- They are Lewis bases.

- They may be anions or neutral molecules.

Examples:

(i) $K_4[Fe(CN)_6]$. In this complex compound CN^- (cyanide ion) is anionic ligand
(ii) $[Ag(NH_3)_2]Cl$. In this complex compound NH_3 (Ammine) is a neutral ligand

(b) Coordination Sphere

"The central metal atom or ion along with ligands is called coordination sphere".

- It is usually placed in square brackets.
- It may be anionic, cationic or neutral.

Examples:

(i) $K_4[Fe(CN)_6]$. In this complex compound, $[Fe(CN)_6]^{4-}$ is the anionic coordination sphere.
(ii) $[Cu(NH_3)_4]SO_4$. In this complex compound, $[Cu(NH_3)_4]^{2+}$ is the cationic coordination sphere.
(iii) $[Ni(CO)_4]$. In this complex compound, $[Ni(CO)_4]^0$ is the neutral coordination sphere.

(c) Coordination Number

"The number of lone pair of electrons provided by the ligands to the central metal atom or ion is called the coordination number of the central metal atom or ion".

Examples:

(i) $K_4[Fe(CN)_6]$. In this complex compound, the coordination number of iron is 6.
(ii) $[Cu(NH_3)_4]SO_4$. In this complex compound, the coordination no. of copper is 4.

(d) Central Metal Ion or atom

"A metal atom or ion usually a transition element surrounded by a number of ligands is called central metal atom or ion"

Examples:

(i) $K_4[Fe(CN)_6]$. Fe^{++} is the central metal ion.
(ii) $[Ag(NH_3)_2]Cl$, Ag^+ is the central metal ion.
(iii) $[Cu(NH_3)_4]SO_4$, Cu^{2+} is a central metal ion.

(e) Charge on the coordination sphere

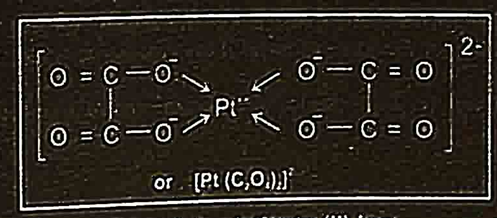
It is the algebraic sum of the charges present on the central metal ion and the total charge on the ligands.
$[Fe(CN)_6]^{4-}$

Charge on iron	= +2
Total charge on six CN^- ions	= −6
Charge on the coordination sphere	= −6 + 2 = −4

(f) Chelates

"When all the donor atoms of a polydentate ligand get coordinated with the same metal ion, a complex compound is formed which contains one or more rings in its structure and is called chelate".

Examples:



or $[Pt(C_2O_4)_2]^{2-}$

Dioxalato platinate (II) ion

When two oxalate ligands $C_2O_4^{2-}$ (bidentate ligand) get coordinated with Pt^{++} ion, dioxalato palatinate (II) ion is formed. In this way, we observe two five membered rings.

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Q. Give some examples of neutral and anionic ligands.

Ans

Neutral Ligands	Anionic Ligands
NH_3 (Ammine)	Cl^- (Chloro), F^- (Fluoro), Br^- (Bromo), I^- (iodo)
H_2O (Aqua)	OH^- (Hydroxo)
CO (Carbonyl)	CN^- Cyano
NO (Nitrosyl)	O^{2-} (Oxido)
PH_3 (Phosphine)	CO_3^{2-} (Carbonato)
CH_3NH_2 (Methylamine)	$(C_2O_4)^{2-}$ (Oxalato)

Q. Classify ligands on the basis of number of electron pairs which they donate.

Ans On the number of electron pairs which they donate, ligands are divided into following types.

Monodentate ligands

"Those ligands which donate one pair of electron to central metal atom or ion are called monodentate ligands."

Examples:

Cl^- (chrloro), Br^- (Bromo), I^- (iodo), CN^- (Cyano), F^- (Fluoro), OH^- (hydroxo), NO_2 (nitro), NO (Nitrosyl), H_2O (aqua), NH_3(ammine) etc.

Bidentate ligands

Those ligands which donate two pairs of electrons to central metal atom or ion are called bidentate ligands.

Examples:

Hydrazine (N_2H_4), $(C_2O_4)^{2-}$ (Oxalato), CO_3^{2-} (Carbonato) etc.

Q.6 Describe the rules for naming the coordination complexes and give examples.

Nomenclature

The nomenclature of complex compounds is based upon the recommendations by the Inorganic Nomenclature Committee of IUPAC.

The rules for naming the complexes are given below.

1. Cations are named before anions.
2. In naming the coordination sphere, ligands are named in alphabetical order regardless of the nature and number of each, followed by the name of central metal ion.
3. The prefixes di, tri, tetra, penta, hexa, etc. are used to specify the number of coordinated ligands.
4. The names of anionic ligands end in suffix "O", e.g. hydroxo, (OH^-), carbonato (CO_3^{2-}).
5. The names of neutral ligands are usually unchanged, e.g. for NH_3, ammine, for H_2O, aqua and for CO, carbonyl.
6. The suffix 'ate' comes at the end of the name of metal if the complex represents an anion, otherwise it remains unchanged.
7. The oxidation number of the metal ion is represented by a Roman numeral in parenthesis following the name of the metal.

Examples

$K_4[Fe(CN)_6]$ Potassium hexacyno ferrate (II)

$[PtCl(NO_2)(NH_3)_4]SO_4$ Tetraammine chloronitro-platinum (IV) sulphate

$[Co(NO_2)_3(NH_3)_3]$ Triammine trinitrocobalt (III)

Writing the formulas of complexes

In writing the formula of a complex ion, the usual practice is to place the symbol of the central metal atom first, followed by the formulas of the ionic ligands in alphabetical order, then neutral ligands in alphabetic order and the formula of the whole complex ion is enclosed in square brackets.

Q.11 Give systematic names to following complexes.

Ans

(a) $[Fe(CO)_5]$, Pentacarbonyl iron(o).

(b) $[Co(NH_3)_6]Cl_3$, Hexa – ammine cobalt(III) chloride

(c) $[Fe(H_2O)_6]^{2+}$, Hexaaqua iron (II) ion

(d) $Na_3[CoF_6]$, Sodium hexaflouro cobaltate (III).

(e) $K_2[Cu(CN)_4]$, Potassiumtetracyano cupparate (II)

(f) $K_2[Pt(Cl_6)]$, Potassium hexachloro palatinate (IV)

(g) $[Pt(OH)_2(NH_3)_4]SO_4$, Tetra – ammine dihydroxoplatinum (IV) sulphate.

(h) $[Cr(OH)_3(H_2O)_3]$, Triaquatrihydroxochromium (III)

Geometry of the complexes

The geometry of complexes depend upon the type of hybridization taking place in the valence shell of central metal atom or ion.

Complex Ion	State of hybridization of the central atom	Shape & Structure
$[MnCl_4]^{2-}$	sp^3	Tetrahedral
$[Cu(NH_3)_4]^{+2}$	dsp^2	Square planar
$[PCl_5]$	dsp^3	Trigonal bipyramidal
$[Co(NH_3)_6]^{3+}$	sp^3d^2	Octahedral

Iron

Iron has been known since prehistoric days. It was used in Egypt in 1500 B.C. It is known that the Chinese also used iron as early as 2500 B.C. In the sub-continent iron was produced around 600 B.C.

Ores of Iron

Magnetite (Fe_3O_4), Haematite (Fe_2O_3) and Limonite ($Fe_2O_3.3H_2O$)

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Commercial Forms of Iron

Iron is available commercially in the following three forms. They differ in carbon contents as follow:

(i) Pig iron or cast iron 2.5 to 4.5% carbon
(ii) Steel 0.25 to 2.5% carbon
(iii) Wrought iron 0.12 to 0.25% carbon

Wrought Iron

Composition

It is the purest form of commercial iron and contains the lowest percentage of carbon and upto 0.3% of impurities like S, P, Si and Mn, etc.

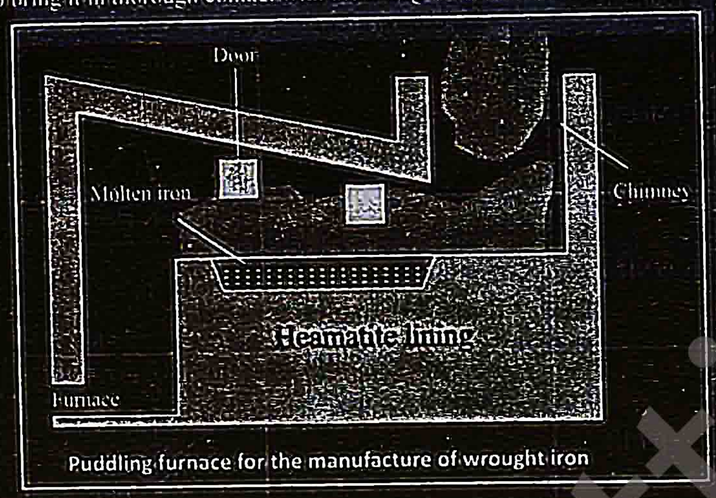
S = 0.2 to 0.15%, Mn = upto 0.25%, P = 0.04 to 0.2%

Manufacture of Wrought Iron from Cast Iron

It is manufactured from cast iron by puddling i.e. by heating cast iron in a special type of reverberatory furnance called puddling furnace.

Puddling Furnance

- This furnace has a low roof to deflect the hot gases and flames downwards and to melt cast iron.
- The hearth of the furnace is lined with hematite (Fe_2O_3).
- The cast iron is placed on the hearth, melted by hot gases and stirred or puddled with long iron rods called rabbles through the doors to bring it in thorough contact with the lining of the hearth, i.e. Fe_2O_3.



Puddling furnace for the manufacture of wrought iron

Oxidation of impurities

The hematite (Fe_2O_3) lining supplies oxygen, necessary for the oxidation of carbon, sulphur, silicon, manganese and phosphorus present in the cast iron.

- Oxides of carbon and sulphur, being volatile escape out at high temperature.

$$3C + Fe_2O_3 \longrightarrow 2Fe + 3CO$$

$$3S + 2Fe_2O_3 \longrightarrow 4Fe + 3SO_2$$

- While those of manganese, silicon and phosphorus form slag. Thus,

$$3Si + 2Fe_2O_3 \longrightarrow 4Fe + 3SiO_2$$

$$2Mn + O_2 \longrightarrow 2MnO$$

$$MnO + SiO_2 \longrightarrow MnSiO_3 \text{ (Slag)}$$

$$4P + 5O_2 \longrightarrow 2P_2O_5$$

$$Fe_2O_3 + P_2O_5 \longrightarrow 2FePO_4 \text{ (Slag)}$$

Collecting the Wrought Iron

With the removal of impurities, the melting point of the metal rises and it becomes a semi-solid mass. At this stage, it is taken out in the form of balls or blooms on the ends of rabbles. While still hot, these balls are subjected to hammering to squeeze out as much of slag as possible. The product so obtained is known as wrought iron.

Steel

Steel is an alloy of iron containing 0.25 to 2.5% of carbon and traces of S, P, Si and Mn.

Classification of Steel

Steel is classified on the basis of percentage of carbon, present in it.

1. Mild Steel (0.1-0.2% C)

- It is fairly soft, malleable and ductile, can be forged (shaped by hammering and pressing while hot).
- It is used in making tubes, nuts, bolts, bars and boiler plates.

2. Medium Carbon Steel (0.2-0.7% C)

- It is harder than mild steel.
- It is also malleable and ductile.
- It is used in making rails, axels, castings.

3. High Carbon Steel (0.7-1.5% C)

- It is hard and can be forged when containing less than 1.0% carbon.
- Steel containing more than 1.0% carbon cannot be forged.
- It is used to make hammers, taps, dies, cutting tools, machine tools, hard steel parts of machinery and all sorts of engines.

Steel is intermediate in carbon contents between cast iron and wrought iron. It can be produced from:

(i) cast iron by removing some carbon along with sulphur, phosphorus and silicon.
(ii). by adding the required amount of carbon to wrought iron, then adding some special constituents, e.g., tungsten, chromium, vanadium, molybdenum, manganese, nickel and cobalt which impart desired properties to the steel. At present most of the steel is manufactured from cast iron.

Manufacture of Steel

It can be manufactured by the following processes:

(a) Open hearth process (using cast iron, wrought iron or steel scrap)
(b) Bessemer's process (using cast iron only)

Some other processes are also used to prepare special type of steel from pure wrought iron.

Open Hearth Process

This is the most modern method for the manufacture of steel. It is carried out in an open hearth furnace. This furnace has a low roof to deflect the hot gases and flames downward to melt the charge. The open hearth furnace works on the regenerative principle of heat economy.

Types

Open hearth process is of two types:

1. Furnace with acidic lining like SiO_2 is used when the impurities are Mn, Si, etc.
2. Furnace with basic lining like dolomite (CaO, MgO) is used when the impurities are P and S, etc.

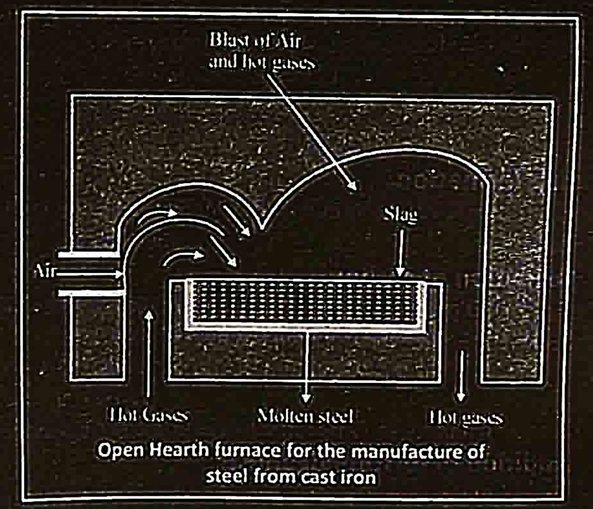
Process

A mixture of cast iron, scrap steel and quick lime is charged into the furnace. At about 1600°C Si, Mn, C, S and P are burnt out and removed according to the following reactions:

$$C + 1/2O_2 \longrightarrow CO$$

$$Si + O_2 \longrightarrow SiO_2$$

$$Mn + 1/2O_2 \longrightarrow MnO$$



Open Hearth furnace for the manufacture of steel from cast iron

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CO escapes in the flue gases. Silica (SiO_2) combines with CaO, MnO and FeO to form silicates (slag) which float on the surface of the molten metal.

$$SiO_2 + CaO \longrightarrow CaSiO_3$$
$$SiO_2 + MnO \longrightarrow MnSiO_3$$
$$SiO_2 + FeO \longrightarrow FeSiO_3$$

Phosphorus and sulphur react with Fe_2O_3 to form P_2O_5 and SO_2 respectively.

$$2Fe_2O_3 + 3S \longrightarrow 4Fe + 3SO_2$$
$$5Fe_2O_3 + 6P \longrightarrow 10Fe + 3P_2O_5$$

These oxides react with calcium oxide to form slag.

$$P_2O_5 + 3CaO \longrightarrow Ca_3(PO_4)_2 \text{(Fertilizer)}$$
$$SO_2 + CaO \longrightarrow CaSO_3$$

Q. What is ferromanganese?

Samples are taken at intervals and the percentage of carbon in the steel is determined regularly. When this is reduced to about 0.1%, the calculated mass of ferromanganese (Fe, Mn, C) is added. Manganese desulphurises the steel. Ferromanganese raises the carbon contents to the required values. After giving time for mixing, a little more ferromanganese is added, and the charge is allowed to run into moulds where it solidifies to ingots.

The whole process takes about 10 hours. Slag contains calcium phosphate, It is ground to powder and sold as a fertilizer.

Q.7 Explain the Bessemer's process for the manufacture of steel.

Bessemer's Process

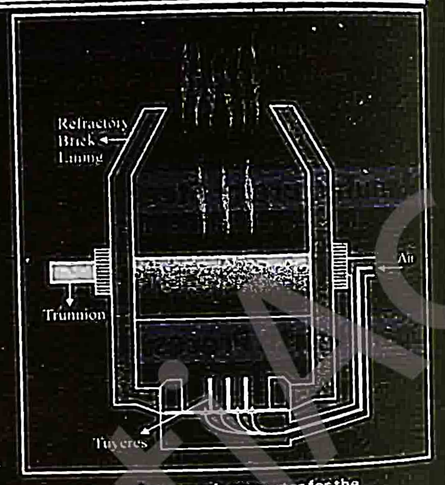
Bessemer's Converter:

- The furnace used in this process is called Bessemer's Converter which is a pear shaped vessel made of steel plates.
- At the bottom the convertor is provided with a number of holes through which hot air is introduced.
- The convertor is held on a central axis so that it can be tilted in any desired position for feeding and pouring out the finished materials.

Feeding the charge:

Molten pig or cast iron (25 to 30 tons) from the blast furnace is fed into the converter and hot air blast is injected through the perforated base. This oxidizes carbon, silicon, and manganese.

$$C + \tfrac{1}{2}O_2 \longrightarrow CO$$
$$Si + O_2 \longrightarrow SiO_2$$
$$2Mn + O_2 \longrightarrow 2MnO$$



Bessemer's converter for the manufacture of steel from cast iron.

Slag formation:

These oxides form a slag of $MnSiO_3$. The heat evolved during the oxidation is enough to keep iron in the molten state.

$$MnO + SiO_2 \longrightarrow MnSiO_3 \text{ (Slag)}$$

Oxidation of carbon:

CO produced burns at the mouth of the converter with a blue flame. Iron is partly oxidized to ferric oxide (Fe_2O_3) which also extracts carbon from cast iron to form CO.

$$4Fe + 3O_2 \longrightarrow 2Fe_2O_3$$
$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

Within 10 to 15 minutes the flame due to CO subsides indicating that the carbon is completely oxidized.

Addition of ferromanganese:

At this stage ferromanganese is added to correct the proportion of carbon to obtain the desired qualities. A blast of air is continued for a moment to ensure thorough mixing. The addition of Mn imparts increased hardness and tensile strength.

Removal of air bubbles:

In order to remove entraped bubbles of gases (blow holes), such as O_2, N_2, CO_2, a little aluminium or ferro-silicon is also added. Aluminium removes nitrogen as nitride.

$$2Al + N_2 \longrightarrow 2AlN$$

At the end of the operation, the molten steel is poured out into moulds for casting. Such casting are free from any defect.

Corrosion

"Any process of chemical decay of metals due to the action of surrounding medium is called corrosion."

Causes of Corrosion

(i) By gases: The simplest case of corrosion occurs when metals come into contact with gases of the atmosphere. The surface of metals becomes coated with compounds such as oxides, sulphides and carbonates. Such compounds sometime form a compact layer on the surface protecting the metal from further attack e.g., Al.

(ii) By Water: The case would be different when the metal is in contact with water. The compounds formed in this case may dissolve in water, allowing the corrosion to penetrate further into the metal. Besides dissolving the compounds, water also promotes electrochemical process which is one of the main causes of rapid corrosion.

Q. Describe electrochemical theory for the process of corrosion.

Ans: ## Electrochemical Theory

- Pure metals are not easily corroded, even iron hardly gets corroded if absolutely pure. The impurities present in the metal promote corrosion.
- To understand why impurities accelerate the corrosion of metals, consider what happens when two different metals come in contact with one another in moist air. Suppose, for instance, Cu is brought in contact with Al. After sometime, we shall notice that aluminium gets corroded while copper remains intact. This can be explained by the electrochemical theory.
- According to this theory, moisture and CO_2 are present on the surface of the metal. Water ionizes into H^+ and OH^- ions. CO_2 dissolves in water forming H_2CO_3 which ionizes as follows:

$$CO_2 + H_2O \longrightarrow H_2CO_3$$
$$H_2CO_3 \rightleftharpoons H^+ + HCO^-_3$$

Copper and aluminium are, in a sense, immersed in the solution containing H^+, OH^- and HCO_3^- ions.

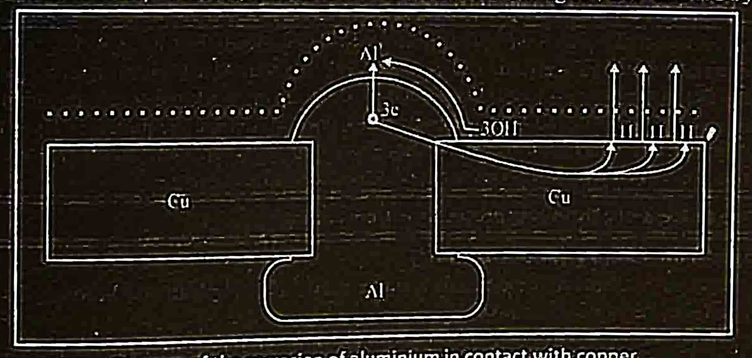


Diagram of the corrosion of aluminium in contact with copper

This forms a galvanic cell in which aluminium releases electrons and changes to Al^{+3} ion (being more reactive than (Cu) i.e., it acts as negative electrode and Cu acts as a positive electrode.

Anode

$$Al \longrightarrow Al^{3+} + 3e^-$$
$$Al^{3+} + 3OH^- \longrightarrow Al(OH)_3$$

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Aluminium ions attract OH^- ion to form $Al(OH)_3$ i.e., it starts dissolving.

Cathode

$$2H^+ + 2e \longrightarrow H_2$$

The H^+ ions present on the Cu receive the electrons and released as H_2.

Conclusion

In this way aluminium corrodes rapidly when in contact with copper which is lower in electrochemical series. From this we can conclude that when an active metal Al (higher in the electrochemical series) comes in contact with less active metal Cu (lower in the electrochemical series); a galvanic cell is established. In this process active metal corrodes rapidly while the other intact.

Prevention of Corrosion

It has been observed that the amount of iron destroyed each year by corrosion equals to about one-fourth of its annual production. It is therefore necessary to prevent such a damaging process and avoid this loss.

Different methods are used to prevent corrosion:

(i) The simplest method of protecting the surface of matter from coming in direct contact with the surrounding by coating it with oil, paint, varnish or enamel.

(ii) It can be prevented by alloying the metals.

(iii) It can also be prevented by coating the metal with a thin layer of another metal, e.g., Tin plating, galvanizing.

Q.8 (a) Why does damaged tin plated iron get rusted quickly?

Ans **Tin plating or coating iron with tin (cathode coating)**

The process of tin plating consists of dipping the clean sheet of iron in a bath of molten tin and then passing it through hot pairs of rollers. Such plates are used in a manufacture of tin canes, oil containers and other similar articles.

Tin itself is a very stable and protects the metals effectively as long as its coating on the iron is intact.

If the protective coating is damaged, then iron comes into contact with moisture. A Galvanic cell is established in which tin acts as a cathode and iron as an anode. The electrons flow from iron to tin, where they discharge H^+ ions, leaving behind OH^- in the solution. These OH^- ions react with iron and forming $Fe(OH)_3$, which dissolves rapidly in water.

$$Fe^{3+} + 3OH^- \longrightarrow Fe(OH)_3$$

From this, it can be concluded that plated iron gets rust more rapidly when the protective coating is damaged than the non – plated iron.

Q.8 (b) Under what conditions does aluminium corrode?

Ans When an active metal Al comes in contact with less active metals like Zn, Cu, Fe, Sn (i.e. having greater reduction potential than Al) a Galvanic cell is established in which Al acts as an anode while metals like Zn, Fe etc act as cathode. In this process, active metal (Al) corrodes rapidly while the others remain intact.

On the other hand, the main condition of rapid corrosion of Al is when the protected layer is damaged and the metal comes in direct contact with water. Besides dissolving the compounds, water also allow the corrosion to penetrate further into the metal and promotes the electro chemical process.

Q.8 (c) How does the process of galvanizing protect iron from rusting?

Ans **Galvanizing or Zinc Coating (anode coating)**

Galvanizing is done by dipping a clean iron sheet in a zinc chloride bath and heating. The iron sheet is then removed, rolled into Zn bath and air cooled.

In this case, If a protective layer of zinc is damaged, a galvanic cell is established in the presence of moisture. Iron serves as a cathode and zinc as an anode. Electrons flow from Zn to iron, as a result of which Zn decays while Fe remains intact. This is called **sacrificial corrosion.**

$$Fe^{+2} + Zn \longrightarrow Zn^{+2} + Fe$$

This is the way, galvanizing helps protecting iron from rust. This process used in water pipes etc.

Chromates and Dichromates

Chromates and dichromates are the salts of chromic acid, H_2CrO_4, and dichromic acid, $H_2Cr_2O_7$, respectively. Both Acids exist only in aqueous solution and when attempts are made to isolate them from solution, they decompose immediately into chromic anhydride (Cr_2O_3) and water. Their salts are, however, quite stable.

Potassium Chromate (K_2CrO_4)

Q. Describe the preparation of K_2CrO_4.

Preparation of K_2CrO_4

1. The chromates of alkali metals, which are soluble in water, are obtained by oxidizing trivalent chromium compounds in the presence of an alkali.

$$2KCrO_2 + 3Br_2 + 8KOH \longrightarrow 2K_2CrO_4 + 6KBr + 4H_2O$$

2. Chromates can also be produced by fusing Cr_2O_3 with an alkali in the presence of an oxidant, such as potassium chlorate.

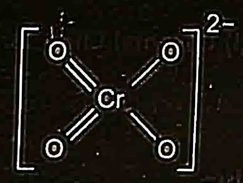
$$Cr_2O_3 + 4KOH + KClO_3 \longrightarrow 2K_2CrO_4 + KCl + 2H_2O$$

3. Chromates are usually prepared from natural chromite ($FeO.Cr_2O_3$), if it is strongly heated with potassium carbonate in the presence of the oxygen. The resulting fused mass will contain potassium chromate which can be extracted with water.

$$4FeCr_2O_4 + 8K_2CO_3 + 7O_2 \longrightarrow 8K_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

Properties

Structure of Chromate ion



Almost all the chromates are yellow in colour. Some of them are used as pigments. For instance, insoluble lead chromate, $PbCrO_4$, is employed for the preparation of yellow oil colour called yellow crown.

Q. How dichromate ions are converted into Chromate ions?

Ans In an aqueous solution, CrO_4^{2-} and $Cr_2O_7^{2-}$ exist in equilibrium.

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

When an alkali is added in this sol., the OH^- ions from the alkali Binds the H^+ ions in solution to form H_2O. Thus according to le-Chatelier's principle when conc. of reactants decrease then the reaction / equilibrium will shift in the backward direction so in this way, the dichromate ion $Cr_2O_7^{2-}$ can be converted into chromate ion CrO_4^{2-}

Q.9 How chromate ions are converted into dichromate ions?

Ans In an aqueous solution, CrO_4^{2-} and $Cr_2O_7^{2-}$ ion exist in equilibrium.

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

When an acid is added in such a sol. then the H^+ ions from the acid increases in its conc. According to Le-Chatelier's principle, if the conc. of reactants increased at equilibrium stage this will disturbs the position and the reaction is shifted in forward direction. So in this way, CrO_4^{2-} ions are converted into dichromate ions. $Cr_2O_7^{2-}$

Potassium Dichromate ($K_2Cr_2O_7$) (Surkh Kahi)

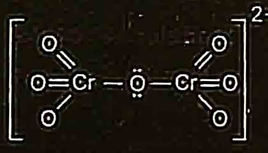
Preparation

1. K_2CrO_4 is converted to $K_2Cr_2O_7$ by using H_2SO_4. By adding an acid to aqueous solution of K_2CrO_4 equilibrium will shift in the forward direction *i.e.*, changing chromate ions into dichromate ions.

$$2K_2CrO_4 + H_2SO_4 \rightleftharpoons K_2Cr_2O_7 + K_2SO_4 + H_2O$$

2. Sometimes sodium dichromate is converted into potassium dichromate by reacting it with KCl.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$



Properties

Physical Properties

- It is an orange red crystalline solid
- It melts at 396°C.
- It is fairly soluble in water.

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$K_2Cr_2O_7$ as an Oxidizing agent

Dichromates are very powerful oxidizing agents. Oxidation is carried out in an acid solution. In this process, hexavalent chromium ion is reduced to trivalent chromium ion.

(a) Reaction with H_2S

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$3H_2S + 3[O] \longrightarrow 3H_2O + 3S$$

$$K_2Cr_2O_7 + 3H_2S + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$

(b) Reaction with Ferrous Sulphate

Potassium dichromate oxidizes ferrous sulphate to ferric sulphate in the presence of sulphuric acid.

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

(c) Reaction with Potassium Iodide

Potassium dichromate also oxidizes KI in the presence of H_2SO_4.

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$$

(d) Chromyl Chloride Test

When solid potassium dichromate is heated with solid metal chloride in the presence of concentrated sulphuric acid chromyl chloride is produced.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$$

Uses

(a) $K_2Cr_2O_7$ finds extensive use in dyeing.
(b) It is used in leather industries for chrome tanning.
(c) It is used as an oxidizing agent.

Potassium Permanganate ($KMnO_4$)

This compound is the salt of permanganic acid, $HMnO_4$. It is an unstable acid and exists only in solution.

Q. Describe the preparation of $KMnO_4$.

Preparation of $KMnO_4$

It is prepared by acidifying the solution of potassium manganate, K_2MnO_4 by H_2SO_4.

$$3K_2MnO_4 + 2H_2SO_4 \longrightarrow 2K_2SO_4 + 2KMnO_4 + MnO_2 + 2H_2O$$

On a large-scale, it is prepared from the mineral pyrolusite, MnO_2. The finely powdered mineral is fused with KOH in the presence of air or an oxidizing agent like KNO_3 or $KClO_3$ etc. This treatment gives us green coloured potassium manganate, K_2MnO_4, in fused state.

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

$$MnO_2 + 2KOH + KNO_3 \longrightarrow K_2MnO_4 + KNO_2 + H_2O$$

$$3MnO_2 + 6KOH + KClO_3 \longrightarrow 3K_2MnO_4 + KCl + 3H_2O$$

The fused potassium manganate K_2MnO_4 obtained as above is extracted with water and the solution, after filtration, is converted into potassium permanganate ($KMnO_4$) by any of the following methods.

(a) Stadeler's Process:

In this method, Cl_2 is passed through the green solution of K_2MnO_4 until it becomes purple due to the formation of $KMnO_4$. Here Cl_2 oxidizes K_2MnO_4 into $KMnO_4$.

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KCl + 2KMnO_4$$

(b)

In this process CO_2 is passed through the green solution of K_2MnO_4 until it becomes purple.

$$3K_2MnO_4 + 2H_2O + 4CO_2 \longrightarrow 2KMnO_4 + MnO_2 + 4KHCO_3$$

(c) Electrolytic Oxidation Process

In this process manganate is converted into permanganate by electrolytic oxidation. During electrolysis of an aqueous solution of K_2MnO_4, water is decomposed to evolve hydrogen gas at the cathode and oxygen gas at the anode. Oxygen liberated at the anode, oxidizes magnate ion $(MnO_4)^{2-}$ into permanganate ion $(MnO_4)^{1-}$ while hydrogen is liberated at the cathode.

$$2K_2MnO_4 + H_2O + [O] \longrightarrow 2KMnO_4 + 2KOH$$

The purple solution of $KMnO_4$ obtained as above is filtered through asbestos, concentrated and allowed to crystallize when $KMnO_4$ deposits as deep purple-red rhombic prisms.

Properties

1. Potassium permanganate forms dark purple lustrous crystals giving deep pink colour in solution.
2. Its solubility in water at 20°C is only about 7% while it dissolves more at higher temperature (25% at 63°C).



Structure of permangnate ion

$KMnO_4$ as an Oxidizing Agent

Potassium permanganate is a powerful oxidizing agent. Oxidation is usually carried out in an acid solution.

(a) Reaction with H_2S

It oxidizes H_2S to sulphur.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$5H_2S + 5[O] \longrightarrow 5H_2O + 5S$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + 2MnSO_4 + 5S + 8H_2O$$

(b) Reaction with $FeSO_4$

It oxidizes $FeSO_4$ to $Fe_2(SO_4)_3$.

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

(c) Reaction with oxalic acid

It oxidizes oxalic acid to CO_2 and H_2O on heating.

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

(d) Reaction with KOH

When an alkaline solution of $KMnO_4$ is heated, O_2 is evolved.

$$4KMnO_4 + 4KOH \longrightarrow 4K_2MnO_4 + 2H_2O + O_2$$

Uses

It is used
(i) as an oxidizing agent.
(ii) as a disinfectant and a germicide.
(iii) in the manufacture of many organic compounds.

KEY POINTS

1. Transition elements have partially filled d or f subshells in atomic state or in any of their commonly occurring oxidation states.
2. II-B and III-B group elements are called non-typical transition elements.

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3. Binding energies, melting points, paramagnetism and oxidation states of transition metals increase with increasing number of unpaired electrons.
4. Such compounds containing the complex molecules or complex ions and capable of independent existence are called coordination compounds or complex compounds.
5. When a complex ion absorbs a wavelength from visible light, it transmits a set of radiation that impart colour.
6. Wrought iron contains 0.12% - 0.25% carbon while steel contains 0.25% -2.25% carbon.
7. Chromate and dichromate ions exist in equilibrium in an aqueous solution.
8. Chemical decay of metals under the action of their surrounding medium is called corrosion. It can be prevented by tin plating and galvanizing.

SOLVED OBJECTIVE EXERCISE

Q1. Fill in the blanks.

(i) The property of paramagnetism is due to the presence of _____ electrons.
(ii) MnO_4^- ion has ___ colour and $Cr_2O_7^{2-}$ has ___ colour.
(iii) When potassium chromate is treated with an acid _____ is produced.
(iv) The d-block elements are located between _____ and _____ block elements.
(v) Oxidation number of Fe in $K_4[Fe(CN)_6]$ is _____ while in $K_3[Fe(CN)_6]$ it is _____.
(vi) The presence of _____ in a metal promotes corrosion.
(vii) If copper is in contact with aluminum, _____ gets corroded.
(viii) Complexes having sp^3d^2 hybridization have _____ shape.
(ix) In naming the complexes, all the ligands are named in ___
(x) In an aqueous solution CrO_4^{-2} and $Cr_2O_7^{2-}$ exist in the form of _____.

Answer Key.

(i)	Unpaired	(ii)	Purple, orange red
(iii)	$K_2Cr_2O_7$	(iv)	s, p
(v)	+2, +3	(vi)	Impurities
(vii)	Aluminium	(viii)	Octahedral
(ix)	Alphabetical order	(x)	Equilibrium

Q2. Indicate True or false.

(i) A substance which is attracted into a magnetic field is said to be diamagnetic.
(ii) Compounds of the transition elements are mostly coloured.
(iii) Fe^{3+} ions are blue when hydrated.
(iv) An extreme case of paramagnetism is called diamagnetism.
(v) Tin plating is used to protect iron sheets from corrosion
(vi) In galvanizing zinc prevents corrosions of iron.
(vii) Tin plated iron gets rusted more rapidly when the protective coating is damaged than the unplated iron.
(viii) The name of anionic ligands in a complex ends in suffix, O.
(ix) Pig iron contains greater percentage of carbon that steel.
(x) Complex compounds having dsp^2 hybridization have tetrahedral geometry.

Answer Key.

(i)	False	(ii)	True	(iii)	False	(iv)	False	(v)	True
(vi)	True	(vii)	True	(viii)	True	(ix)	True	(x)	False

Q3. Multiple Choice Questions. Encircle the correct answer.

(i) Which of the following is a non-typical transition element?
(a) Cr (b) Mn (c) Zn (d) Fe

(ii) Which of the following is a typical transitions metal?
(a) Sc (b) Y (c) Ra (d) Co

(iii) f-Block elements are also called
(a) non-typical transition element (b) outer transition elements
(c) Normal transition elements (d) None is true

(iv) The strength of binding energy of transition elements depends upon
(a) number of electron pairs (b) number of unpaired electrons
(c) number of neutrons (d) number of protons

(v) Group VIB of transition elements contains
(a) Zn,Cd,Hg, (b) Fe, Ru, Os (c) Cr, Mo,W (d) Mn,Te, Re

(vi) Which is the formula of tetraaminechloronitroplatinum (IV) sulphate?
(a) $[Pt(NH_3)_4(NO_2)]SO_4$ (b) $[PtNO_2Cl(NH_3)_4]SO_4$
(c) $[PtCl(NO_2)(NH_3)_4]SO_4$ (d) $[Pt(NH_3)_4(NO_2)Cl]SO_4$

(vii) The percentage of carbon in different types of iron products is in the order of
(a) cast iron > wrought iron > steel (b) wrought iron > steel > cast iron
(c) cast iron > steel > wrought iron (d) cast iron = steel > wrought iron

(viii) The colour of transition metal complexes is due to
(a) d-d transitions of electrons (b) paramagnetic nature of transition elements.
(c) ionization (d) loss of s- electrons.

(ix) Coordination number of Pt in $[Pt\,Cl(NO_2)(NH_3)_4]^{2+}$ is
(a) 2 (b) 4 (c) 1 (d) 6

(x) The total number of transition elements is
(a) 10 (b) 30 (c) 40 (d) 58

Solved Exercise MCQ's

(i)	(c) Zn	Zn does not have a partially filled d-orbital either as element or in any of its oxidation state, so it is non-typical transition element.
(ii)	(d) Co	Sc and Y are non-typical transition elements, Ra is not a transition element but Co is a typical transition element.
(iii)	(d) None is true	f – Block elements are inner transition elements.
(iv)	(b) Number of unpaired electrons	Greater the number of unpaired electrons, greater the binding energy.
(v)	(c) Cr, Mo,W	Group VI B elements are typical transition elements.
(vi)	(c) $[Pt\,Cl(NO_2)(NH_3)_4]SO_4$	Pt is central metal atom and Cl, NO_2 and NH_3 are ligands.
(vii)	(c) Cast iron > Steel > wrought iron	Wrought iron is the purest form of iron having least percentage of carbon.
(viii)	(a) d – d transitions of electrons	When d-orbitals are involved in bonding, they split up into two energy levels, one set has a higher energy than the other. Electrons residing in low energy d-orbitals absorb a part of visible light and jump to high energy d-orbitals.
(ix)	(d) 6	Cl, NO_2 and NH_3 are monodentate ligands so donate one electron pair to Pt each. Hence, coordination number of Pt is 6.
(x)	(d) 58	It includes both d and f – block elements.

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Previous Board Questions

1. What is Coordination Sphere? Give examples.
2. Discuss Galvanizing Process.
3. Define these:
   (a) Paramegnetism (b) Substitutional Alloys
4. Give the systematic names of these complexes:
   (a) $K_2[Cu(CN)_4]$ (b) $[Pt(OH)_2(NH_3)_4]SO_4$
5. What is meant by sacrificial corrosion?
6. Under what conditions does aluminium corrode?
7. Why damaged tin plated Can should be avoided?
8. Write chemical formula of: (i) Potassium Hexacynao Ferrate (II) (ii) TriamminoTrinitro cobalt (III)
9. What are chelates? Explain with an example.
10. Why transition elements compounds are coloured?
11. What is meant by typical and non-typical transition elements?
12. Why most of the transition metal ions are coloured?
13. "$KMnO_4$ is a strong oxidizing agent". Support the statement with two chemical reactions.
14. What are interstitial compounds?
15. Why does damaged tin plated iron gets rusted quickly?
16. What are
    (a) Co-ordination number (b) Central metal atom
17. Give systematic names of the following complexes
    (a) $Na_3[CoF_6]$ (b) $K_2[Cu(CN)_4]$
18. Why Fe^{++} shows strongest paramagnetic behavior?
19. Give two methods of preparation of $K_2Cr_2O_7$.
20. Why transition elements usually show more than one oxidation states in their compounds?
21. Why the maximum paramagnetic strength is associated with the middle elements of d-block series?
22. How does the metallic coating prevent the corrosion?
23. Write the equation of chromyl chloride test for KCl.
24. Write two balanced equations for the preparation of $K_2Cr_2O_7$.
25. Write balanced equation in which $K_2Cr_2O_7$ oxidizes KI in the presence of H_2SO_4.

For Answers study
Scholar's CHEMISTRY (Objective) XII
⇒ MCQ's
⇒ Entry Test MCQ's
⇒ MCQ's From Past Board Papers
⇒ Additional Short Questions with Answers
⇒ Previous Board papers and Many More in the Objective Chemistry

CHAPTER 7

FUNDAMENTAL PRINCIPLES OF ORGANIC CHEMISTRY

Introduction

More than 200 years ago, early chemists separated organic compounds from inorganic compounds due to the differences in their origin and properties. Chemical compounds are of two types:

(i) Organic compounds (Old Definition)

The compounds obtained from living things, plants or animals were considered as organic compounds e.g. butter, cheese, cotton, silk, glucose etc.

(ii) Inorganic compounds

The compounds obtained from non-living or mineral sources were called inorganic compounds.

e.g. NaCl, $CaCO_3$, H_2SO_4 etc.

Vital Force Theory

This theory was introduced by J.Berzelius in 1815 According to this theory:

"Organic compounds can be manufactured only by and within the living things and these compounds can never be synthesized from inorganic materials in laboratory."

Scientist	Preparation	Compound
Wohler (1828)	By heating ammonium cyanate	Urea
Kolbe (1845)	From elements and hydrogen	Acetic acid
Berthelot (1856)	By heating barium formate	Methane

Q. What is the importance of Wohler's work in the development of organic chemistry?

Ans

Wohler's work

Friedrick Wohler was a German chemist. He rejected the vital force theory. When he obtained urea $(NH_2)_2CO$, an organic compound in the urine of mammals, from ammonium cyanate, NH_4CNO, a substance of known mineral origin.

$$\underset{\text{Ammonium cyanate}}{NH_4CNO} \rightleftharpoons \underset{\text{Urea}}{(NH_2)_2CO}$$

Since the synthesis of urea, millions of organic compounds have been prepared and analyzed. In this way organic chemistry made progress by leaps and bounds.

Q. What is vital force theory? Who rejected this theory?

Organic Compounds (Modern Definition)

"All those compounds which contain carbon as an essential element along with hydrogen, oxygen, nitrogen, sulphur, phosphorus, halogens, etc. are called organic compounds." e.g., Glucose, methane, benzene etc.

- For historical and conventional reasons a few of the carbon compounds such as CO, CO_2, carbonates, bicarbonates, etc are studied as inorganic compounds.
- In the same way, diamond and graphite which are allotropes of carbon are inorganic compounds.
- It also has been recognized that the chemical forces in organic compounds are similar to those, which exist, in inorganic compounds.

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Organic Chemistry (Modern Definition)

"Organic chemistry is that branch of chemistry which deals with the study of compounds of carbon and hydrogen (hydrocarbons) and their derivatives."

Some Features of Organic Compounds

Following are some features of organic compounds.

(1) Peculiar Nature of Carbon

Carbon forms a large number of compounds. There are millions of organic compounds known at present. The main reason for such a large number of compounds is its unique property of linking with other carbon atoms to form long chains or rings. This self-linking property of carbon is called **catenation.**



Carbon also forms stable single and multiple bonds with other atoms like oxygen, nitrogen and sulphur, etc. It can thus form numerous compounds of various sizes, shapes and structures.

(2) Non-ionic Character of Organic Compounds

Organic compounds are generally covalent compounds, because organic compounds contain carbon. Carbon belongs to fourth group of the periodic table and forms bonds by sharing. Therefore, do not give ionic reactions.

(3) Similarity in Behaviour

There exists a close relationship between different organic compounds. This is exemplified by the existence of homologous series. This similarity in behaviour has reduced the study of millions of compounds to only a few homologous series.

Homologous Series

A group of chemical compounds which are structurally alike and have same chemical properties. In a homologous series two successive members of the group differ from each other by a ($-CH_2-$) group or a mass of 14 amu.

The members of a homologous series generally have same;

(i) General formula
(ii) Methods of preparation
(iii) Chemical properties
(iv) A gradual change in physical properties

Examples: Alkanes, Alcohols, Ketones, etc.

(4) Complexity of Organic Compounds

Organic molecules are usually large and structurally more complex. For example, starch has the formula $(C_6H_{10}O_5)_n$ where n may be several thousands. Proteins are very complex molecules having molecular masses ranging from a few thousands to a million.

(5) Isomerism

Isomerism is a very common phenomenon in organic compounds. Very often more than one compounds are represented by the same molecular formula. However, they have different structural formulas.

(6) Rates of Organic Reactions

The reactions of organic compounds are slow and in general, the yields are low. The slow rate of the organic reactions is due to the molecular nature of organic compounds.

(7) Solubility

Most organic compounds are insoluble in water and dissolve readily in non-polar organic solvents, such as benzene, petroleum ether, etc.

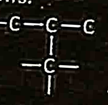
Q. A large number of organic compounds is due to catenation property of carbon. Justify.

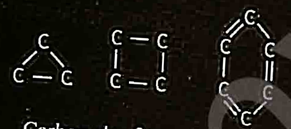
Ans. Catenation:

"The self linking property of an element is called catenation".

Carbon shows maximum catenation property due to high C – C bond energy. Carbon is a unique element and it is essential element of organic compounds. Its unique features are as follows.

(a) C – C – C – C – C – C

(b) 

(c) 

(d) C – C, C = C, C ≡ C

(e) Carbon also forms bonds with H, O, N, S, P, X.

Due to these reasons, a large number of organic compounds is due to catenation property of carbon.

Importance of Organic Chemistry

The importance of organic chemistry can hardly be over emphasized. Almost all the chemical reactions that take place in living systems, including our own bodies, are organic in nature because they involve such life molecules like proteins, enzymes, carbohydrates, lipids, vitamins and nucleic acids, all contain thousand of carbon atoms. We have become dependent upon organic compounds that occur in nature for our food, medicines and clothing. Over the years, the chemists have learned to synthesize plastics, synthetic rubber, medicines, preservatives, paints, varnishes, textile fibres, fertilizers, pesticides, detergents, cosmetics, dyes, etc. Many of these synthetic compounds prevent the shortages of naturally occurring products.

Q.12 Describe important sources of organic compounds.

SOURCES OF ORGANIC COMPOUNDS

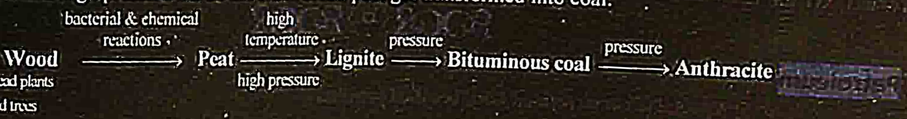
Petroleum, coal and natural gas are main sources of organic compounds. These are called fossil fuels and are formed, over long period of time, from the decay of plants and animals.

Coal

"Coal is a combustible black or brownish-black sedimentary rock usually occurring in rock strata."

Formation of Coal

It is believed that coal in nature was formed from the remains of the trees buried inside the earth crust some 500 millions years ago. Due to the bacterial and chemical reactions on wood it got converted into peat. Then, as a result of high temperature and high pressure inside the earth crust, peat got transformed into coal.

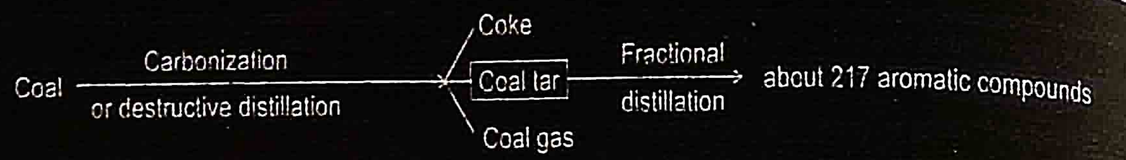


Coal is an important solid fuel and becomes a source of organic compounds when subjected to carbonization or destructive distillation.

Carbonization (Destructive Distillation) of Coal

"When coal is heated at high temperature (500-1000° C) in the absence of air, it is converted into coke, coal gas and coal tar".

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Coal tar contains a large number of aromatic organic compounds, which separate out on fractional distillation.

Uses of Coal

The total coal resources of Pakistan are estimated by the geological survey of Pakistan to be 184 billion tonnes. Following are some uses of coal:

(i) About 80% of this coal is used to bake bricks in lime kilns.

(ii) Some quantity is used for domestic purposes.

Development of Coal in Pakistan

Conscious efforts are being made by the government to induct coal into industry by setting up coal based power units. The Sind Coal Authority and the directorates of Mineral Developments of the Punjab, Baluchistan and NWFP are all keen to expand coal utilization in power generation for which many incentives have been made available.

Natural Gas

"A gaseous mixture of low boiling hydrocarbons which mainly composed of methane is called natural gas".

Composition:

Major portion of the natural gas is methane. Others are ethane, propane and butane. A small amount of CO_2, N_2, H_2S and He are also present in natural gas.

Formation:

It is also formed by the decomposition of organic matter.

Uses of Natural Gas

Natural Gas is an important means of energy especially for countries like Pakistan, which are deficient in the production of mineral oil and coal. It is used:

(i) for power generation.

(ii) in cement and fertilizer industries.

(iii) as a fuel in general industries

(iv) for domestic purposes

(v) as CNG and LNG for automobile fuel.

Petroleum

"Mineral oil in its refined form is called petroleum".

Formation of Petroleum

It is thought to have been formed by slow chemical and biochemical decomposition of the remains of organic matters found between **the sedimentary rocks**. When extracted from rocks it appears like a liquid of blackish colour known as **crude oil**. It is refined to get different petroleum fractions.

Fractional Distillation of Petroleum

The crude petroleum is separated by fractional distillation into a number of fractions each corresponding to a particular boiling range.

Q. Name the fractions which are obtained by Fractional distillation of Petroleum.

Principal Fractions Obtained from Petroleum

Fraction	Boiling Point Range (°C)	Composition	Uses
Natural gas	< 20	CH_4-C_4H_{10}	Fuel, petrochemicals
Petroleum ether	20-60	C_5H_{12}, C_6H_{14}	Solvent
Ligroin, or naphtha	60-100	C_6H_{14}, C_7H_{16}	Solvent, raw material
Gasoline	40-220	C_4H_{10}-$C_{13}H_{28}$ mostly C_6H_{14}-C_8H_{18}	Motor fuel
Kerosene	175-325	C_8H_{18}, $C_{14}H_{30}$	Heating fuel
Gas oil	> 275	$C_{12}H_{26}$, $C_{18}H_{38}$	Diesel and heating fuel
Lubricating oils and greases	Viscous liquids	> $C_{18}H_{38}$	Lubrication
Paraffin	M.p. 50-60	$C_{25}H_{55}$-$C_{29}H_{60}$	Wax products
Asphalt, or petroleum coke	Solids	Residue	Roofing, paving, fuel reducing agent

Oil Refineries in Pakistan

At present four oil refineries are in operation in our country.

- One oil refinery known as Attock Oil Refinery is located at Morgah near Rawalpindi. It has about 1.25 million tonnes oil refining capacity.
- Two oil refineries have been established at Karachi which have about 2.13 million tonnes of oil refining capacity.
- Pak-Arab refinery is located at Mahmud Kot near Multan.

Q10. Write a short note on cracking of hydrocarbons.

Cracking (Pyrolysis) of Petroleum

"Thermal decomposition of higher hydrocarbons having high boiling points into variety of lower hydrocarbons, which are more volatile (low boiling) is called cracking."

Example

A higher hydrocarbons $C_{16}H_{34}$ (hexadecane) cracks according to the following reaction.

$$C_{16}H_{34} \xrightarrow[700^\circ C]{\text{Heat}} C_7H_{16} + 3CH_2 = CH_2 + CH_3 - CH = CH_2$$

Hexadecane Heptane Ethene Propene

This is the process in which C-C bonds in long chain alkane molecules are broken, producing smaller molecules of both alkanes and alkenes. The composition of the products depends on the condition under which the cracking takes place.

Types of Cracking

Cracking is generally carried out in the following ways.

(1) Thermal Cracking

Breaking down of large molecules by heating at high temperature and pressure is called **Thermal Cracking.**

Nature of Product:

It is particularly useful in the production of **unsaturated hydrocarbons** such as ethene and propene.

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(2) Catalytic Cracking

Higher hydrocarbons can be cracked at lower temperature (500°C) and lower pressure (2atm), in the presence of a suitable catalyst. A typical catalyst used for this purpose is a mixture of silica (SiO_2) and alumina (Al_2O_3).

Nature of Product:

Catalytic cracking produces **gasoline** of higher octane number. This method is used for obtaining better quality **gasoline.**

(3) Steam Cracking

In this process, higher hydrocarbons in the vapour phase are mixed with steam, heated for a short duration to about 900°C and cooled rapidly.

Nature of Product:

The process is suitable for obtaining **lower unsaturated hydrocarbons.**

Q. Why there is need of cracking?

Need of Cracking

(i) The fractional distillation of petroleum yields only about 20% gasoline. Due to its high demand this supply is augmented by converting surplus supplies of less desirable petroleum fractions such as kerosene oil and gas oil into gasoline by a process called cracking.

(ii) Besides increasing the yield of gasoline, cracking has also produced large amounts of useful by-products, such as ethene, propene, butene and benzene. These are used for manufacturing drugs, plastics, detergents, synthetic fibres, fertilizers, weed killers and important chemicals like ethanol, phenol and acetone.

Knocking

"The sharp metallic sound produced when low quality fuel burns in internal combustion engine is called knocking."

The gasoline fraction present in petroleum is generally not of good quality. When it burns in an automobile engine, combustion can be initiated before the spark plug fires. This produces a sharp metallic sound called **knocking.** Knocking greatly reduces the efficiency of an engine.

Octane number

"The percentage of branched chain hydrocarbon (Iso-Octane) in gasoline fraction of petroleum is called Octane number."

- A fuel having high Octane number
  (a) is less likely to produce knocking
  (b) burns smoothly in internal combustion engine
  (c) increases the efficiency of engine.
- Iso-octane (2,2,4–Trimethyl pentane) has been arbitrarily given an octane number of 100 while n-heptane has given an octane number zero.

Improvement of Octane number

Octane number of gasoline can be improved by various ways:

(i) Reforming
(ii) Aromatization
(iii) Blending with TEL
(iv) Addition of aromatic compounds (BTX)

Cetane number:

It is used to determine the quality of diesel oil.

Q.11 Explain reforming of petroleum with the help of suitable example?

Ans. **Reforming**

"The thermal conversion of straight chain hydrocarbons into branched chain hydrocarbon in the absence of oxygen (air) and in the presence of a catalyst is called reforming".

$$CH_3-(CH_2)_6-CH_3 \xrightarrow[\text{Catalyst}]{\text{Heat}} CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-\underset{\displaystyle CH_3}{\overset{|}{CH}}-CH_3$$

n-octane → 2,2,4-Trimethylpentane (Iso-octane)

- This method is used for improving octane number of gasoline.

Q. **What is TEL? Describe its role as knocking inhibitor? Or How TEL improves octane number of gasoline. Also give its disadvantage.**

Ans **Tetra ethyl lead (TEL)**

The octane number of a poor fuel can also be improved by blending it with a small amount of additive like tetraethyl lead (TEL). Tetraethyl lead $(C_2H_5)_4Pb$, is an efficient antiknock agent.

Disadvantages of TEL

TEL has one serious disadvantage; its combustion product, lead oxide, is reduced to metallic lead which is discharged into the air through the exhaust pipe and causes air pollution. It causes blindness and mental retardation in infant children.

Q4. **How organic compounds are classified? Give suitable example of each type.**

Ans **CLASSIFICATIONS OF ORGANIC COMPOUNDS**

There are millions of organic compounds. It is practically not possible to study each individual compound. To facilitate their study, organic compounds are classified into various groups and sub-groups. They may be broadly classified into the following classes.

(i) Open chain or Acyclic compounds.
(ii) Closed chain or Cyclic (or ring) compounds.

(i) Open Chain or Acyclic Compounds

This type of compounds contain an open chain of carbon atoms. The chains may be branched or non-branched (straight chain). The open chain compounds are also called aliphatic compounds.

Straight Chain (or non- branched) Compounds

Those organic compounds in which the carbon atoms are connected in series from one to the other.

$CH_3-CH_2-CH_2-CH_3$ n-Butane

$H_2C=CH-CH_2-CH_3$ 1–Butene

$CH_3-CH_2-CH_2-CH_2-OH$ 1– Butanol

Branched chain compounds

Those organic compounds in which the carbon atoms are attached on the sides of chain.

$$CH_3-\underset{\displaystyle CH_3}{\overset{|}{CH}}-CH_3$$ 2-Methyl propane (Iso-butane)

$$CH_3-C(=CH_2)-CH_3$$ 2-Methylpropene

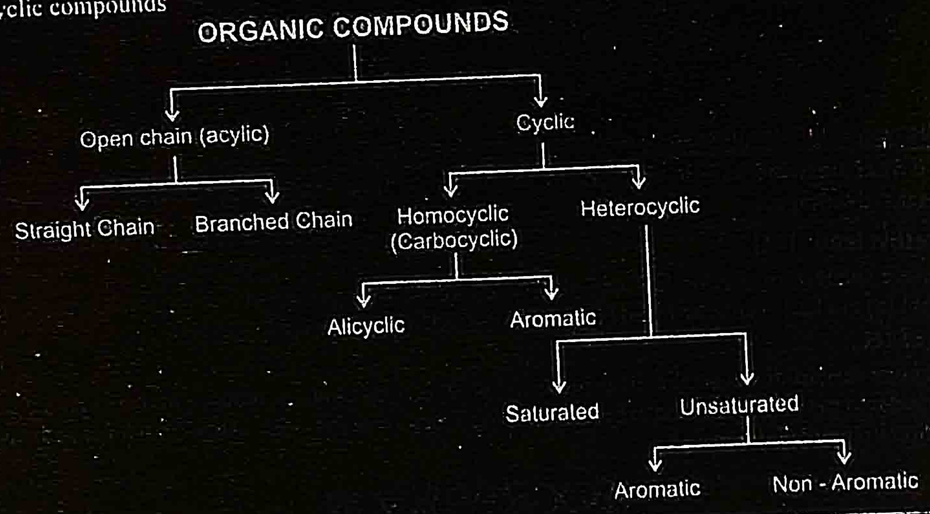
$$CH_3-\underset{\displaystyle CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3$$ 2,2-Dimethyl propane (neo-pentane)

(ii) Closed Chain Compounds or Cyclic Compounds

These compounds contain closed chains or rings of atoms and are known as cyclic or ring compounds. These are of two types;

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(a) Homocyclic or carbocyclic compounds
(b) Heterocyclic compounds



Q.5 What are homocyclic and heterocyclic compounds? Give one example of each type.

Ans. Homocyclic or Carbocyclic Compounds

"The compounds, in which the ring consists of only carbon atoms, are called homocyclic or carbocyclic compounds".

Homocyclic or carbocyclic compounds are further classified as:

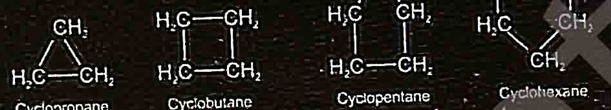
(i) Alicyclic compounds (ii) Aromatic compounds

(i) Alicyclic Compounds

The homocyclic compounds which contain a ring of three or more carbon atoms and resembling aliphatic compounds are called alicyclic compounds.

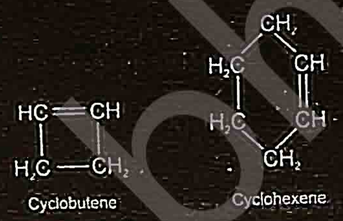
- The saturated alicyclic hydrocarbons (cycloalkanes) have the general formula C_nH_{2n}.

Examples:



- One or more hydrogen atoms present in these compounds may be substituted by other group or groups.
- The unsaturated alicyclic hydrocarbons (cycloalkenes) have the general formula C_nH_{2n-2}.

Examples:



(ii) Aromatic Compounds

These carbocyclic compounds contain at least one benzene ring, (six carbon atoms with three alternate double and single bonds) is called aromatic compounds.

MCQ'S

The general formula of cycloalkane is a similar as that of

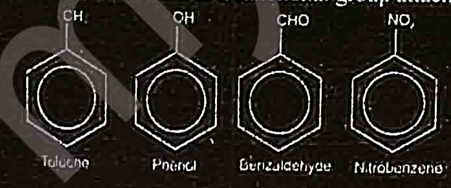
(a) Alkane (b) Alkene
(c) Alkyne (d) Alcohol

Examples:

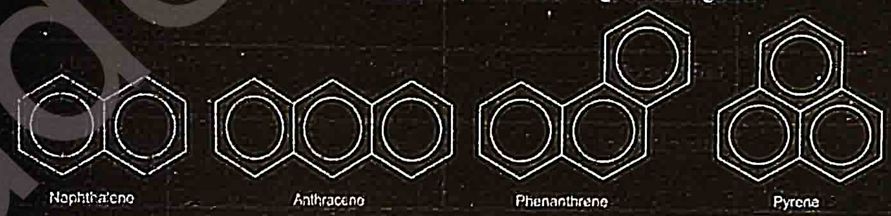
(a)



(b) The aromatic compounds may have a side-chain or a functional group attached to the ring. For example:



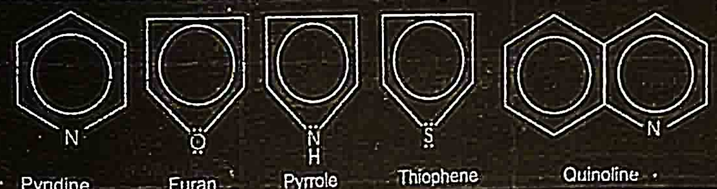
(c) The aromatic compounds may also contain more than one benzene rings fused together.



(b) Heterocyclic Compounds

The compounds in which the ring consists of atoms of more than one kind are called heterocyclic compounds or heterocycles. In heterocyclic compounds generally one or more atoms of elements such as nitrogen (N), oxygen (O) or sulphur (S) are present.

- The atom other than carbon such as. N, O, or S, present in the ring is called a **hetero atom.**



According to **Huckle rule**, pyridine, Furan, Pyrrole, Thiophene etc are non-benzenoid **aromatic compounds.**

Board Questions:

Q1. Differentiate between homocyclic and heterocyclic organic compounds?
Q2. Differentiate between alicyclic and aromatic organic compounds?

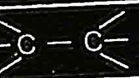
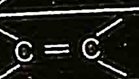
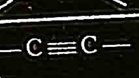
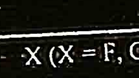
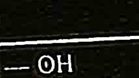
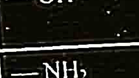
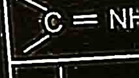
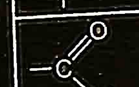
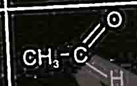
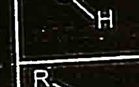
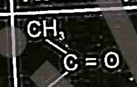
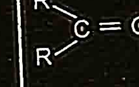
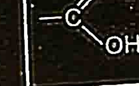
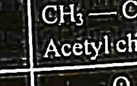
Q.8 What is meant by a functional group? Name typical functional groups containing oxygen.

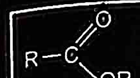
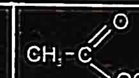
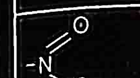
Ans. **Functional Group**

"An atom or a group of atoms or a double bond or a triple bond whose presence imparts specific properties to organic compounds is called a functional group."

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- They are the chemically functional parts of molecules.
- Each functional group defines an organic family.

Functional group		Class of compounds	Examples
Formula	Name		
	None	Alkane	$CH_3 - CH_3$ Ethane
	Double bond	Alkene	$H_2C = CH_2$ Ethene
	Triple bond	Alkyne	$HC \equiv CH$ Ethyne
	Halo: (fluoro, chloro, bromo, iodo)	Alkyl halide	$CH_3 - CH_2 - Cl$ Ethyl chloride
	Hydroxyl group	Alcohol or alkanol	$CH_3–CH_2–OH$ Ethanol
	Amino group	Amine	$CH_3–CH_2–NH_2$ Ethyl amine
	Imino group	Imine	$CH_2 = NH$ Methylimine
	Ether linkage	Ether	$CH_3–CH_2–O–CH_2–CH_3$ Diethyl ether
	Formyl group	Aldehyde or alkanal	 Acetaldehyde
	Carbonyl	Ketone or alkanone	 Acetone
	Carboxyl group	Carboxylic acid (or alkanoic acid)	 Acetic acid
	Acid halide	Acid halide	 Acetyl chloride
	Acid amide	Acid amide	 Acetamide

	Ester group	Ester	 Methyl acetate
– SH	Mercapto	Thioalcohol or Thiol	$CH_3–CH_2–SH$
– C ≡ N	Cyano	Alkyl cyanide or Alkane nitrile	$CH_3 — C \equiv N$ Methyl cyanide
	Nitro	Nitro compounds	$C_6H_5NO_2$ Nitro benzene

Q.13 What is orbital hybridization? Explain Sp^3, Sp^2, and Sp modes of hybridization of carbon.

Hybridization of Orbitals and the Shapes of Molecules

Although the most stable electronic configuration of a carbon atom (having two partially filled 2p orbitals) requires it to be divalent, carbon is tetravalent in the majority of its compounds. In order to explain this apparent anamoly, it is assumed that an electron from the 2s orbital is promoted to an empty 2p, orbital, giving the electronic configuration:

Ground state electronic configuration of carbon = $1s^2, 2s^2, 2p^1_x, 2p^1_y, 2p^0_z$

Excited state electronic configuration of carbon = $1s^2, 2s^1, 2p^1_x, 2p^1_y, 2p^1_z$

The excited state configuration can explain the tetravalency of carbon but these four valencies will not be equivalent. Orbital hybridization theory has been developed to explain the equivalent tetravalency of carbon.

According to this theory the four atomic orbitals of carbon belonging to valence shell may be mixed in different ways to explain the bonding and shapes of molecules formed by carbon atoms.

sp^3 Hybridization

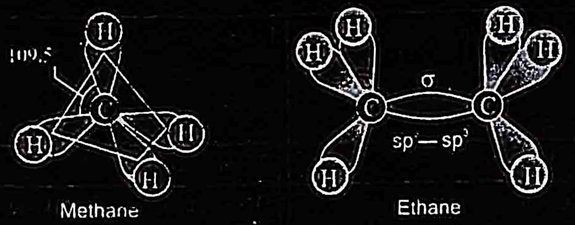
In order to explain the bonding and shapes of molecules in which carbon is attached with four atoms, all these four atomic orbitals are mixed together to give rise to four new equivalent hybrid atomic orbitals having same shape and energy. This mode of hybridization is called tetrahedral or sp^3 hybridization.



All these four sp^3 hybrid orbitals are degenerate (having equal energy) and are directed at an angle of 109.5 in space to give a tetrahedral geometry.

When a carbon atom forms single bonds with other atoms, these hybrid orbitals overlap with the orbitals of these atoms to form four sigma bonds. This type of hybridization explains the bonding and shapes of all those compounds in which carbon atom is saturated.

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Methane Ethane

In the formation of methane, the four hybrid atomic orbitals of carbon overlap separately with four 1s atomic orbitals of hydrogen to form four equivalent C-H bonds. The shape of methane is tetrahedral. All the four hydrogen atoms do not lie in the same plane.

Atomic orbitals of slightly different energy mix up (i.e. one s and three p) to give four sp^3 hybrid (degenerate) orbitals which has same energy and shape is called sp^3 hybirdization. It explain the shape and bonding of the molecules.

In ethane, CH_3-CH_3, the two tetrahedrons of each carbon are joined together. Further addition of a carbon atom with ethane will mean the attachment of another tetrahedron.

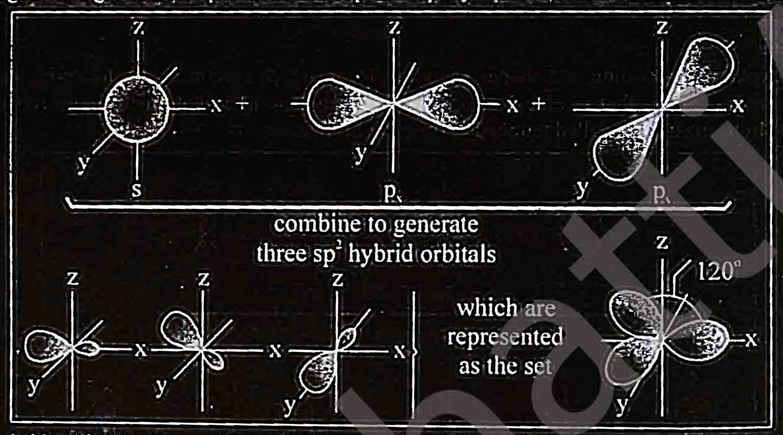
Q. From where does the energy come to excite the carbon atom?

The answer to this question is simple. Before excitation the carbon should make two covalent bonds releasing an adequate amount of energy. After excitation, however, it will form four covalent bonds releasing almost double the amount of energy. This excess energy is more than that needed to excite the carbon atom. So a tetravalent carbon atom is expected to be more stable than a divalent carbon atom.

sp^2 Hybridization

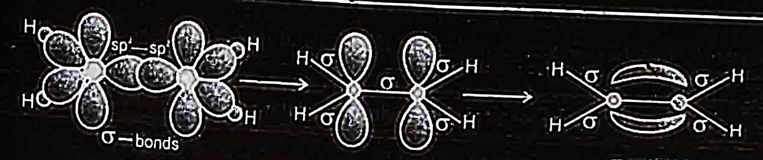
In order to explain the bonding in unsaturated compounds, two more modes of hybridization have been developed.

The structure of alkenes can be explained by sp^2 mode of hybridizaton. In this type one 2s and two 2p orbitals of carbon are mixed together to give three equivalent and coplanar sp^2 hybridized orbitals.



Each sp^2 hybrid orbital is directed from the centre of an equilateral triangle to its three corners. The bond angle between any two sp^2 hybrid orbitals is 120°. The unhybridized $2p_z$ orbital will remain perpendicular to the triangle thus formed.

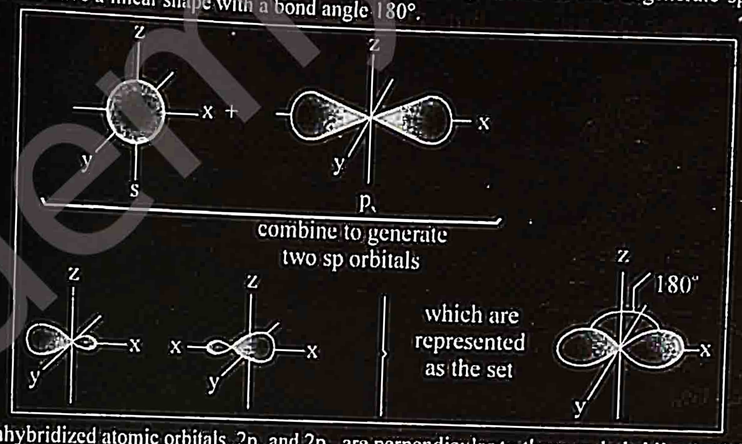
In the formation of ethene molecule, three sp^2 orbitals of each carbon atom overlap separately with sp^2 orbital of another carbon and 1s orbitals of two hydrogen atoms to form three σ bonds. This gives rise to what is called the σ-frame work of ethene molecule. The unhybridized orbitals of each carbon atom will then overlap in a parallel fashion to form a π-bond.



Formation of ethene

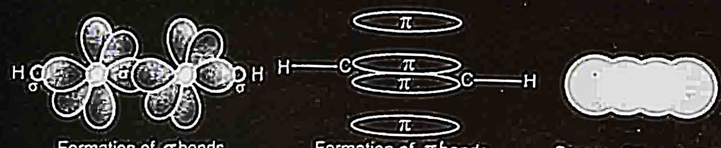
sp-Hybridization

The structure of alkynes can be explained by yet another mode of hybridization called **sp hybridization.** In this type one 2s and one 2p orbitals of the carbon atom mix together to give rise to two degenerate sp hybridized atomic orbitals. These orbitals have a linear shape with a bond angle 180°.



The two unhybridized atomic orbitals, $2p_y$ and $2p_z$, are perpendicular to these sp hybridized orbitals.

Ethyne molecule is formed when two sp hybridized carbon atoms join together to from a σ-bond by sp-sp overlap. The other sp orbital is utilized to form a σ- bond with 1s orbital of hydrogen atom.



Formation of ethyne

The two unhybridized p orbitals on a carbon atom will overlap separately with the p orbitals of the other carbon atom to give two π-bonds both perpendicular to the σ-framework of ethyne. The presence of a σ and two π bonds between two carbon atoms is responsible for shortening the bond distance.

Q.7 Why is ethene an important industrial chemical?

Ans

Importance of Ethene

Ethene is used

(i) For the manufacture of polythene; a plastic material used for making toys, cables, bags, boxes etc.

(ii) For artificial ripening of fruits.

(iii) As a general anaesthetic.

(iv) For preparing mustard gas.

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(v) As a starting material for a large number of chemicals of industrial use such as glycols (antifreeze), ethyl halide and ethyl alcohol etc.

Q.14 Explain the type of bonds and shapes of the following molecules using hybridization approach.

CH_3-CH_3, $CH_2=CH_2$, $CH \equiv CH$, HCHO, CH_3Cl

Ans **(i) Ethane (H_3C-CH_3)**

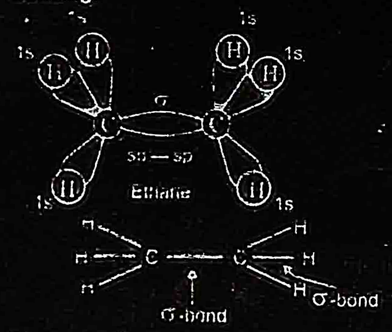
Central atom = C

$_6C = 1s^2, 2s^2, 2p^1_x, 2p^1_y, 2p^0_z$ (Ground state)

$_6C = 1s^2, 2s^1, 2p^1_x, 2p^1_y, 2p^1_z$ (Excited state)

$_6C = 1s^2, sp^3, sp^3, sp^3, sp^3$ (Hybridized state)

Bonding:



(ii) Ethene ($H_2C=CH_2$)

Central atom = C

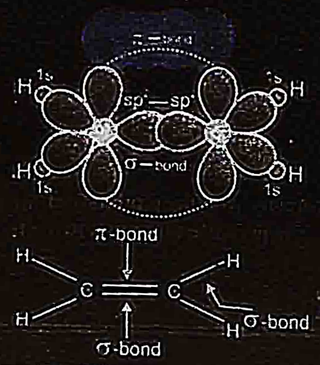
$_6C = 1s^2, 2s^2, 2p^1_x, 2p^1_y, 2p^0_z$ (Ground state)

$_6C = 1s^2, 2s^1, 2p^1_x, 2p^1_y, 2p^1_z$ (Excited state)

Hybridization: sp^2

$_6C = 1s^2, sp^2, sp^2, sp^2, 2p_z$ (Hybridized state)

Bonding:



(iii) Ethyne ($HC \equiv CH$)

Central atom = C

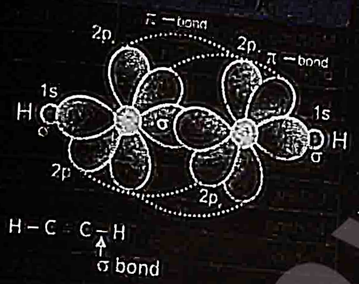
$_6C = 1s^2, 2s^2, 2p^1_x, 2p^1_y, 2p^0_z$ (Ground state)

$_6C = 1s^2, 2s^1, 2p^1_x, 2p^1_y, 2p^1_z$ (Excited state)

Hybridization: sp^2

$_6C = 1s^2, sp, sp, 2p_y, 2p_z$ (Hybridized state)

Bonding:



(iv) Formaldehyde: $H-\overset{O}{\overset{\|}{C}}-H$

Central atom = C

$_6C = 1s^2, 2s^2, 2p^1_x, 2p^1_y, 2p^0_z$ (Ground state)

$_6C = 1s^2, 2s^1, 2p^1_x, 2p^1_y, 2p^1_z$ (Excited state)

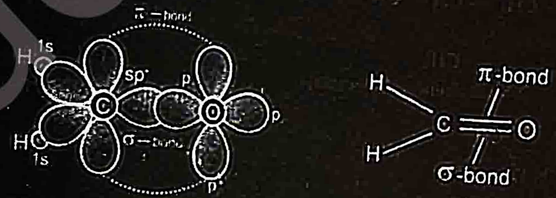
Hybridization: sp^2

$_6C = 1s^2, sp^2, sp^2, sp^2, 2p_z$ (Hybridized state)

$_8O = 1s^2, 2s^2, 2p^4$

$_8O = 1s^2, 2p_x, 2p_y, 2p_z$

Bonding:



(v) Methyl chloride: CH_3Cl

Central atom = C

$_6C = 1s^2, 2s^2, 2p^1_x, 2p^1_y, 2p^0_z$ (Ground state)

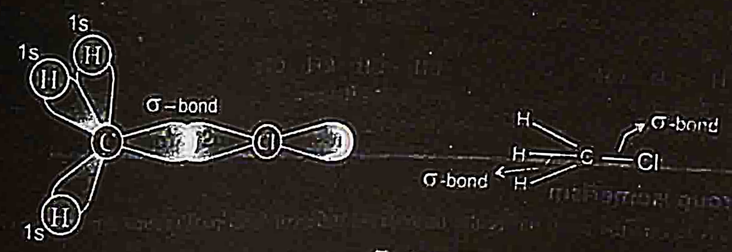
$_6C = 1s^2, 2s^1, 2p^1_x, 2p^1_y, 2p^1_z$ (Excited state)

$_6C = 1s^2, sp^3, sp^3, sp^3, sp^3$ (Hybridized state)

$_{17}Cl = 1s^2, 2s^2, 2p^6, 3s^2, 3p^5$

$_{17}Cl = 1s^2, 2s^2, 2p^6, 3s^2, 3p^1_x, 3p^1_y, 3p^1_z$

Bonding:



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ISOMERISM

"Two or more compounds having the same molecular formula but different structural formulas and properties are said to be isomers and the phenomenon is called isomerism."

- The structural formula of a compound shows the arrangement of atoms and bonds present in it.
- The isomers have different physical properties.

Alkanes		No. of Isomers
Methane, Ethane, Propane		No Isomers
Butane	(C_4H_{10})	2
Pentane	(C_5H_{12})	3
Hexane	(C_6H_{14})	5
Heptane	(C_7H_{16})	9
Octane	(C_8H_{18})	18
Nonane	(C_9H_{20})	35
Decane	($C_{10}H_{22}$)	75
Icosane	($C_{20}H_{42}$)	366319
Squalane	($C_{30}H_{62}$)	more than 4 billions
Tetracontane	($C_{40}H_{82}$)	625 Trillions

Types of Isomerism

(1) Structural Isomerism

(2) Geometric Isomerism

(a) Structural Isomerism

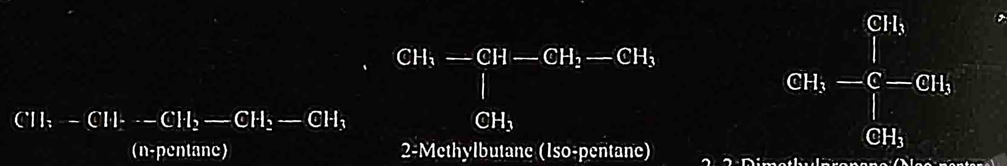
The structural isomerism arises due to the difference in the arrangement of atoms within the molecule. The structural isomerism can be exhibited in five different ways. These are:

(1) The Chain Isomerism

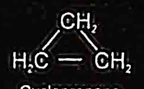
This type of isomerism arises due to the difference in the nature of the carbon chain.

Examples

C_5H_{12}:



C_3H_6: $H_2C = CH - CH_3$ Propene



(2) Position Isomerism

This type of isomerism arises due to the difference in the position of the same functional group on the carbon chain. The arrangement of carbon atoms remains the same.

Examples

C_3H_7Cl:



C_4H_8:

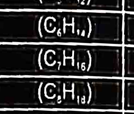
(3) Functional Group Isomerism

The compounds having the same molecular formula but different functional groups are said to exhibit functional group isomerism.

Examples

C_2H_6O: $CH_3 - O - CH_3$ Dimethyl ether; $CH_3 - CH_2 - OH$ Ethyl alcohol

C_3H_6O:



Formula	Functional Isomers
(i) C_nH_{2n}	Alkene and cycloalkane
(ii) C_nH_{2n-2}	Alkadiene and alkyne; cycloalkene
(iii) $C_nH_{2n+2}O$	Alcohol, ether
(iv) $C_nH_{2n}O$	Aldehyde, ketone
(v) $C_nH_{2n}O_2$	Acid, ester, hydroxy aldehyde and hydroxy ketone

(4) Metamerism

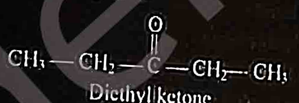
This type of isomerism arises due to the unequal distribution of carbon atoms on either side of the functional group.

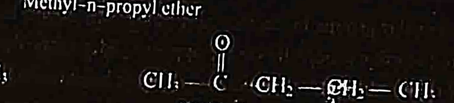
- Such compounds belong to the same homologous series.
- It is due to the presence of different alkyl groups attached to the same polyvalent functional group or atom. i.e., – O –, – S –, – NH –, –CO –.

Examples

$C_4H_{10}O$: $CH_3 - CH_2 - O - CH_2 - CH_3$ Diethyl ether; $CH_3 - O - CH_2 - CH_2 - CH_3$ Methyl-n-propyl ether

$C_5H_{10}O$:

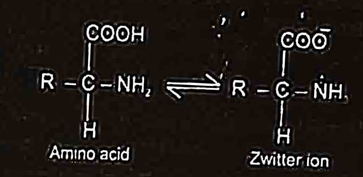




(5) Tautomerism

This type of isomerism arises due to shifting of proton (H') from one atom to other in the same molecule.

Examples





(b) Cis-trans Isomerism (Geometric Isomerism)

"Those compounds which possess the same structural formula, but differ with respect to the positions of the identical groups in space are called cis-trans isomers and the phenomenon is known as the cis-trans or geometric isomerism."

Two carbon atoms joined by a single bond are capable of free rotation about it. However, when two carbon atoms are joined by a double bond, they cannot rotate freely. As a result, the relative positions of the various groups attached to these carbon atoms get fixed and gives rise to cis- trans isomers.

Necessary Conditions

The necessary and sufficient condition for a compound to exhibit geometric isomerism is that the two groups attached to the same carbon must be different.

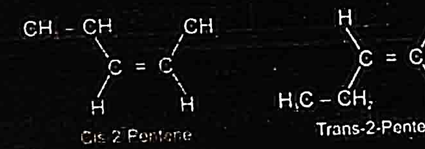
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Examples

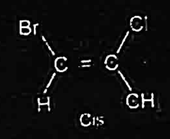
C_4H_8:

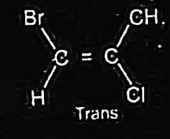


C_5H_{10}:



C_3H_4BrCl:





1-Bromo-2-chlororpopene

- In the cis-form, the similar groups lie on the same side of the double bond.
- In the trans-form, the similar groups lie on the opposite sides of the double bond.

The rotation of two carbon atoms joined by a double bond could happen only if the π bond breaks. This ordinarily costs too much energy, making geometric isomers possible.

MCQ's

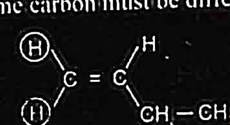
Which of the following will show geometrical isomerism?

(a) C_2H_5Br
(b) $CH_2(COOH)_2$
(c) $(CH)_2(COOH)_2$
(d) C_2H_6

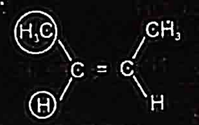
Q. Why is restricted rotation necessary to show the geometrical isomerism? Or 2–Butene does show cis–trans isomerism but 1–Butene does not. Give reason?

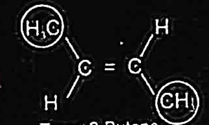
Necessary Conditions

The necessary and sufficient condition for a compound to exhibit geometric isomerism is that the two groups attached to the same carbon must be different.



$H_2C=CH-CH_2-CH_3$
1-Butene



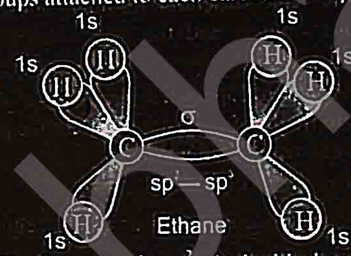


$H_3C-CH=CH-CH_3$
2-Butene

The above structures show that in 1–Butene doubly bonded carbon atom contains two similar atoms attached to one side so unable to show geometric isomerism. On the other hand 2–Butane does show cis–trans isomerism.

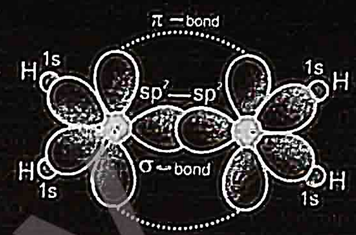
Q.15 Why there is no free rotation around a double bond and a free rotation around a single bond? Discuss cis-trans isomerism.

Ans Whenever two carbon atoms combine with each other by a sigma bond, the hybridization is sp^3. A single bond is formed by the linear overlap of sp^3 orbitals of two carbon atoms. Due to which a sigma electron density is formed between the two nuclei and the groups attached to each carbon are capable of free rotation.



While in double bond the hybridization state is sp^2. A double bond contain a sigma and a pi bond. A sigma electron density is between the two nuclei while the π electron density is formed above & below the line joining

the two nuclei which causes hindrance in the movement of attached groups. Therefore, there is no rotation around a double bond.



Q.6 Write the structural formulas of the two possible isomers of C_4H_{10}.

Ans (i) $CH_3-CH_2-CH_2-CH_3$ n-Butane

(ii) $CH_3-CH(CH_3)-CH_3$ iso-butane

KEY POINTS

1. Chemical compounds were classified as organic and inorganic compounds based upon their origin. Organic compounds are obtained from living things were as inorganic compounds are obtained from mineral sources.
2. It was thought that organic compounds could not be synthesized in the laboratory from inorganic sources.
3. Organic chemistry is now-a-days defined as the chemistry of carbon compounds.
4. Most of the commercially important compounds we use everyday are organic in nature.
5. Coal, petroleum and natural gas are important sources of organic compounds.
6. The process of cracking is developed to increase the yield of lower hydrocarbons which serve as important fuels commercially.
7. Organic compounds are classified into acyclic and cyclic compounds.
8. The study of organic chemistry is organized around functional groups. Each functional group defines an organic family.
9. The type of bonding and the shapes of different type of compounds formed by carbon can be explained by sp^3, sp^2 and sp modes of hybridization.
10. Compounds having the same molecular formula but different structural formulas are called isomers. There are four different type of structural isomers.
11. Isomerism arises due to restricted rotation around a carbon-carbon double bond is called cis-trans isomerism.

SOLVED OBJECTIVE EXERCISE

Q1. Fill in the blanks.

(i) Organic compounds having, same molecular formula but different _____ are called isomers.
(ii) The state of hybridization of carbon atom in _____ is sp^2.
(iii) Alkenes show _____ due to restricted rotation around a carbon – carbon double bound.
(iv) Heating an organic compound in the absence of oxygen and in the presence the _____ as a catalyst is called cracking.
(v) A group of atoms which confers characteristic properties to an organic compound is called _____.
(vi) 2-Butene is _____ of 1–butene.
(vii) Carbonyl functional group is present in both _____ and ketones.
(viii) A heterocyclic compound contains an atom other than _____ in its ring.

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(ix) The quality of gasoline can be checked by finding out its _____.

(x) A carboxylic acid contains _____ as a functional group.

Answer Key.

(i)	Structural formula	(ii)	Ethene
(iii)	Geometric isomerism	(iv)	$SiO_2 + Al_2O_3$
(v)	Functional group	(vi)	Positional isomer
(vii)	Aldehydes	(viii)	Carbon
(ix)	Octane number	(x)	–COOH

Q2. Indicate True or false.

(i) There are three possible isomers for pentane.

(ii) Alkynes do not show the phenomenon of cis-trans isomerism.

(iii) Organic compounds cannot be synthesized from inorganic compounds.

(iv) All closed chain compounds are aromatic in nature.

(v) The functional group present in amides is called an amino group.

(vi) Government of Pakistan is trying to use coal for power generation.

(vii) Crude petroleum is subjected to fractional sublimation in order to separate it into different fractions.

(viii) A bond between carbon and hydrogen serves as a functional group for alkanes.

(ix) o-Nitrotoluene and p-nitrotoluene are the examples of functional group isomerism.

(x) Almost all the chemical reactions taking place in our body are inorganic in nature.

Answer Key.

(i)	True	(ii)	True	(iii)	False	(iv)	False	(v)	False
(vi)	True	(vii)	False	(viii)	False	(ix)	False	(x)	False

Q3. Multiple Choice Questions. Encircle the correct answer.

(i) The state of hybridization of carbon atom in methane is:

(a) sp^3 (b) sp^2 (c) sp (d) dsp^2

(ii) In t-butyl alcohol, the tertiary carbon is bonded to :

(a) two hydrogen atoms (b) three hydrogen atoms

(c) one hydrogen atom (d) no hydrogen atom

(iii) Which set of hybrid orbitals has planar triangular shape?

(a) sp^3 (b) sp (c) sp^2 (d) dsp^2

(iv) The chemist who synthesized urea from ammonium cyanate was:

(a) Berzelius (b) Kolbe (c) Wohler (d) Lavoisier

(v) Linear shape is associated with which set of hybrid orbitals?

(a) sp (b) sp^2 (c) sp^3 (d) dsp^2

(vi) A double bond consists of:

(a) two sigma bonds (b) one sigma and one pi bond

(c) one sigma and two pi bonds (d) two pi bonds

(vii) Ethers show the phenomenon of:

(a) position isomersim (b) functional group isomerism

(c) metamerism (d) cis-trans isomerism

(viii) Select from the following the one which is alcohol:

(a) CH_3-CH_2-OH (b) CH_3-O-CH_3 (c) CH_3COOH (d) CH_3-CH_2-Br

Solved Exercise MCQs

Q.No	Answers	Reasons
(i)	(a) sp^3	Central atom (C) is attached with four H-atoms.
(ii)	(d) no hydrogen atom	Tertiary carbon is attached with no H-atom.
(iii)	(c) sp^2	Angle b/w each orbital is 120°.
(iv)	(c) Wohler	He was a German scientist who rejected vital force theory.
(v)	(a) sp	180° sp sp
(vi)	(b) one sigma and one pi bond	In σ – bond, electronic density lies on the internuclear axis and in π – bond, it lies above and below internuclear axis.
(vii)	(c) metamerism	$CH_3 - CH_2 - O - CH_2 - CH_3$; $CH_3 - CH_2 - CH_2 - O - CH_3$ are metamers.
(viii)	(a) CH_3-CH_2-OH	Alcohol has – OH group as functional group

Previous Board Questions

1. How Coal was formed? Give its importance.
2. What is meant by functional group and functional group isomerism?
3. Why there is no free rotation around a double bond and a free rotation around a single bond?
4. Name the Fractions which are obtained by Fractional distillation of Petroleum.
5. What is cracking of petroleum? Why do we need cracking of petroleum?
6. 1-butene does not show geometrical isomerism but 2-butene exhibit geometrical isomerism. Why?
7. What is Metamarism? Give one example.
8. What are Homocyclic and Heterocyclic compounds? Give one example of each.
9. What are alicyclic compounds? Give two examples.
10. Which organic compound was first of all prepared in the laboratory?
11. How octane numbers of gasoline can be improved by reforming?
12. What is Octane number?
13. Why is restricted rotation necessary to show the geometrical isomerism?

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- Additional Board MCQ's (Answers With Hints)
- Previous Board Short Answers Questions
- Additional Board Short Answers Questions
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CHAPTER 8

ALIPHATIC HYDROCARBONS

Introduction

Hydrocarbons

"Hydrocarbons are organic compounds which contain carbon and hydrogen only." The number of such compounds is very large because of the property of catenation.

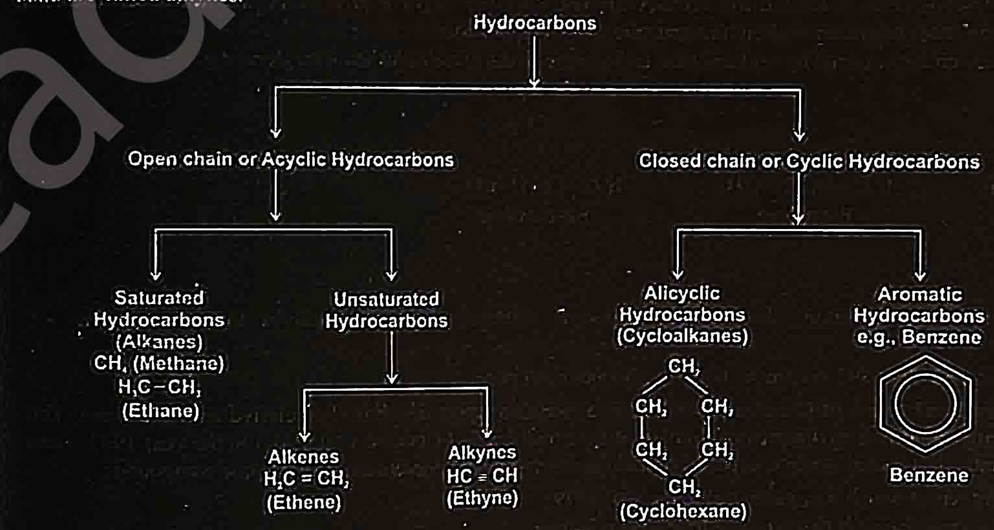
Saturated hydrocarbons or alkanes

If all the valencies of the carbon atoms in a molecule are fully satisfied and these cannot further take up any more hydrogen atoms, then the hydrocarbons are named as saturated hydrocarbons or alkanes.

Unsaturated hydrocarbons

The compounds of carbon and hydrogen in which all the four valencies of carbon are not fully utilized and they contain either a double or a triple bond, such compounds are called unsaturated hydrocarbons.

Those unsaturated hydrocarbons which contain a double bond are called alkenes while those containing a triple bond are called alkynes.



NOMENCLATURE

The system of naming the compound is called nomenclature.

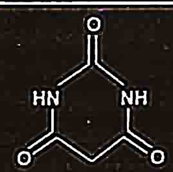
Common or Trivial Names

In the early days, the compounds were named on the basis of

(i) Their history.

(ii) The method of preparation.

(iii) Name of the person working on it.



$C_4H_4N_2O_3$
(Barbituric acid)

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Examples

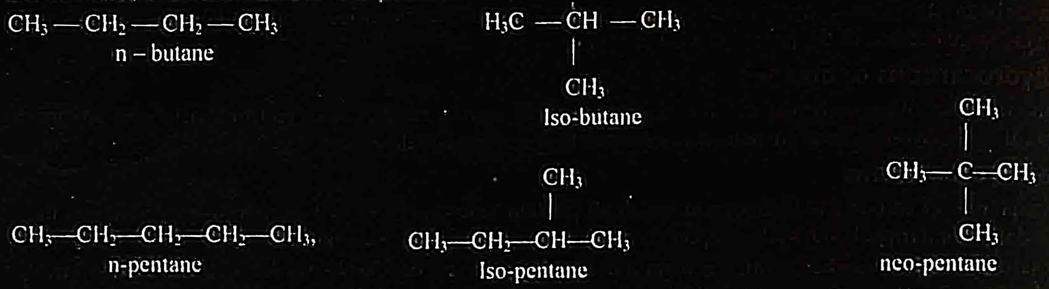
- The name marsh gas was given to methane because it was found in marshy places.
- Acetic acid derives its name from vinegar (Latin, acetum means vinegar).
- Organic compounds were named after a person, like barbituric acid after Barbara.

Such a system may have a certain charm but is never manageable.

Straight and branch chain Hydrocarbons

For alkanes with five or more carbon atoms, the root word is derived from the Greek or Latin numerals indicating the number of carbon atoms in a molecule, and the name is completed by adding 'ane' as a suffix, e.g. pentane (C_5H_{12}), hexane (C_6H_{14}), heptane (C_7H_{16}), etc.

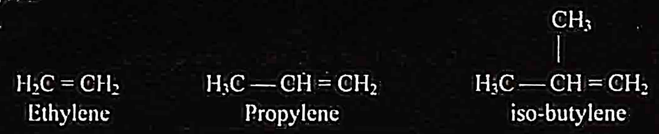
The common or trivial names are applicable to all isomers of a given molecular formula. The prefixes n, iso, neo are, however, to differentiate between isomers.



These prefixes have only limited use, as they are not workable with complex molecules. Moreover, common names give only minimum information about the structure of the compounds.

Alkenes are similarly named by replacing the ending -ane of the name of alkane with ylene. e.g.

Examples



IUPAC Names

- In 1889 the solution for naming the organic compounds systematically was sought by International Chemical Congress.
- A report was accepted in 1892 in Geneva but it was found incomplete.
- In 1930, International Union of Chemistry (IUC) gave a modified report which is also referred as Liege Rules. This report was further modified by International union of Pure and Applied Chemistry (IUPAC) in the year 1947. Since that date the union has issued periodic reports on rules for the systematic nomenclature of organic compounds.
- The most recent report which was published in the year 1979.

IUPAC system of nomenclature is based on the following principle.

'Each different compound should have a different name'.

Thus through a systematic set of rules, the IUPAC system provides different names for more than 7 million known organic compounds.

Nomenclature of Alkyl Groups

If we remove one hydrogen atom from an alkane, the rest of group is called an alkyl group.



- It is represented by '–R'.
- "ane" of alkane is removed by "yl".
- Its general formula is C_nH_{2n+1}.

Alkane	Alkyl Group	Abbreviation
(i) $CH_3 – H$ Methane	CH_3 – Methyl	Me –
(ii) $CH_3 – CH_2 – H$ Ethane	CH_3CH_2 – Ethyl	Et–
(iii) $CH_3–CH_2–CH_2–H$ Propane	$CH_3CH_2CH_2$ – n-Propyl	n-Pr—
(iv) $CH_3–CH(H)–CH_3$ Propane	CH_3CHCH_3 Iso-propyl	iso-Pr—
(v) $H_3C–CH_2–CH_2–CH_2–H$ Butane	$CH_3CH_2CH_2CH_2$ – n-Butyl	n-Bu —

Q. 6. What are the rules for naming alkanes? Explain with suitable examples.

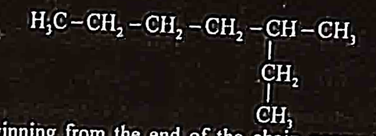
Nomenclature of Alkanes

Branched-chain alkanes are named according to the following rules.

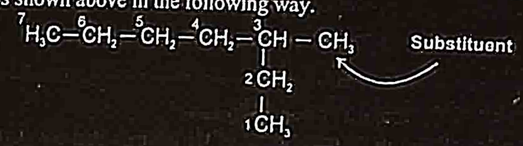
1. Locate the longest continuous chain of carbon atoms; this chain determines the parent name for the alkane. We designate the following compound as a hexane because the longest continuous chain contains six carbon atoms.

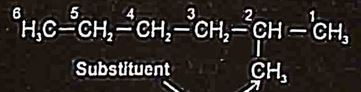


The longest continuous chain may not always be obvious from the way the formula is written. Notice, for example, that the following alkane is designated as a heptane because the longest chain contains seven carbon atoms.



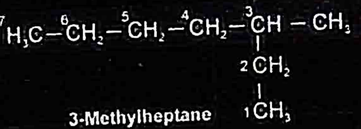
2. Number the longest chain beginning from the end of the chain nearer the substituent. Applying this rule, we number the two alkanes shown above in the following way.



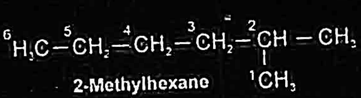


3. Use the numbers obtained by the application of rule 2 to designate the location of the substituent group. The parent name is placed last, and the substituent group, preceded by the number designating its location on the chain, is placed first. Numbers are separated from words by a hyphen. The systematic names of the two compounds shown above will then be:

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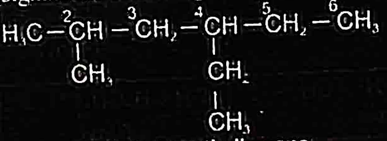


3-Methylheptane



2-Methylhexane

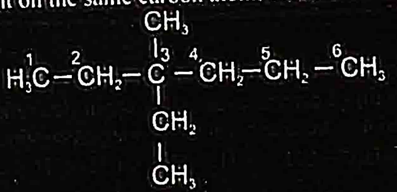
4. When two or more substituents are present, give each substituent a number corresponding to its location on the longest chain. For example, we designate the following compound as 4-ethyl-2-methylhexane.



4-Ethyl - 2-methylhexane

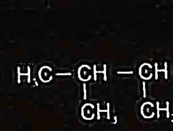
The substituent groups should be listed alphabetically (i.e. ethyl before methyl). In deciding on alphabetical order disregard multiplying prefixes such as "di" and "tri".

5. When two substituents are present on the same carbon atom, use that number twice.

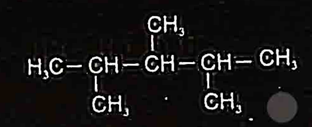


3 - Ethyl - 3 - methylhexane

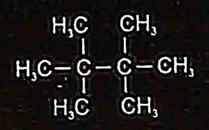
6. When two or more substituents are identical, indicate this by the use of the prefixes di, tri, tetra, and so on. Then make certain that each and every substituent has a number. Commas are used to separate numbers from each other.



2, 3 - Dimethylbutane



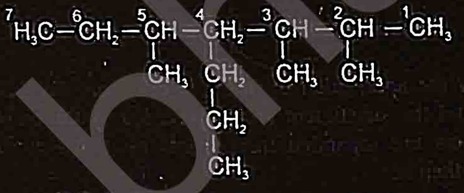
2, 3, 4 - Trimethylpentane



2, 2, 3, 3 - Tetramethylbutane

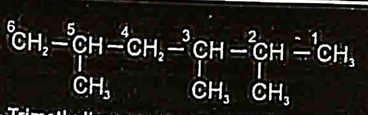
Application of these six rules allows us to name most of the alkanes that we shall encounter. Two other rules, however, may be required occasionally.

7. When two chains of equal length compete for selection as the parent chain, choose the chain with the greater number of substituents.



2, 3, 5 - Trimethyl - 4 - n - propylheptane

8. When branching first occurs at an equal distance from either end of the longest chain, choose the name that gives the lower number at the first point of difference.

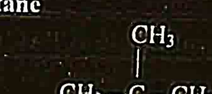
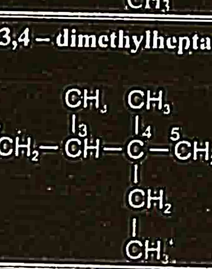
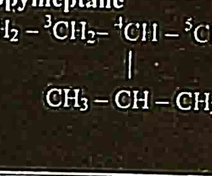
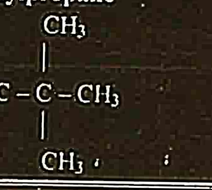


2, 3, 5 - Trimethylhexane (not 2, 4, 5 - Trimethylhexane)

Q4. Write the structural formula for each of the following compounds.

(i) 2-Methylpropane (ii) Neo-pentane.
(iii) 3-Ethylpentane (iv) 4-Ethyl - 3,4 – dimethylheptane.
(v) 2,2,3,4 – Tetramethylpentane (vi) 4-isó – propylheptane.
(vii) 2,2-Dimethylbutane. (viii) 2,2-Dimethylpropane

Ans.

(i)	**2-Methylpropane** 	(ii)	**Neo-pentane**
(iii)	**3-Ethylpentane** 	(iv)	**4-Ethyl - 3,4 – dimethylheptane**
(v)	**2,2,3,4 - Tetramethylpentane** 	(vi)	**4-iso – propylheptane**
(vii)	**2,2-Dimethylbutane** 	(viii)	**2,2-Dimethylpropane**

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Q5. Write down names of the following compounds according to IUPAC system.

(i)	$H_3C-CH_2-CH(CH_2CH_3)-CH_3$	(ii)	$(CH_3)_3C-CH_2-C(CH_3)_3$
(iii)	$H_3C-CH(CH_3)-CH_2-CH(CH_3)-CH_3$	(iv)	$(CH_3)_2CH-CH(CH_3)-CH(CH_3)_2$
(v)	$CH_3CH_2C(CH_3)_2CH(CH_2CH_3)CH_3$	(vi)	$(CH_3CH_2)_3CH$
(vii)	$CH_3C(CH_3)_2(CH_2)_2CH_3$	(viii)	$(C_6H_5)_3CH$

Ans. Names according to IUPAC system.

(i)	$H_3C-CH_2-CH(CH_2CH_3)-CH_3$ **3- Ethylpentane**	(ii)	$CH_3-C(CH_3)_2-CH_2-C(CH_3)_3$ 2,2,4,4 – Tetramethylpentane
(iii)	$H_3C-CH(CH_3)-CH_2-CH(CH_3)-CH_3$ 2,4 – Dimethylpentane	(iv)	$HC(CH_3)_2-CH(CH_3)-CH(CH_3)_2$ 2,3,4 - Trimethylpentane
(v)	$H_3C-CH_2-C(CH_3)_2-CH(CH_3)-CH_3$ CH_3CH_2 CH_3 3, 3, 4 – Trimethylhexane	(vi)	$CH_3-CH_2-CH(CH_2CH_3)-CH_2CH_3$ **3-Ethylpentane**
(vii)	$CH_3-C(CH_3)_2-CH_2-CH_3$ 2,2 -Dimethylpentane	(viii)	$(C_6H_5)_2CH-C_6H_5$ Triphenylmethane

Q7. (a) Write down the structural formulas for all the isomeric hexanes and name them according to IUPAC system.

Ans. (a) Structural formulas and names for all isomeric hexanes.

(i)	$^1CH_3-^2CH_2-^3CH_2-^4CH_2-^5CH_2-^6CH_3$ n-Hexane	(ii)	$^1CH_3-^2CH(CH_3)-^3CH_2-^4CH_2-^5CH_3$ 2 – Methylpentane
(iii)	$^1CH_3-^2CH_2-^3CH(CH_3)-^4CH_2-^5CH_3$ 3 – Methylpentane	(iv)	$^1CH_3-^2C(CH_3)_2-^3CH_2-^4CH_3$ 2,2 – Dimethylbutane
(v)	$^1CH_3-^2CH(CH_3)-^3CH(CH_3)-^4CH_3$ 2,3 – Dimethylbutane		

Q.7(b) The following names are incorrect. Give the correct IUPAC names.

(i) 4-Methylpentane
(ii) 3,5,5-Trimethylhexane
(iii) 2-Methyl-3-ethylbutane

Ans. Correct IUPAC names

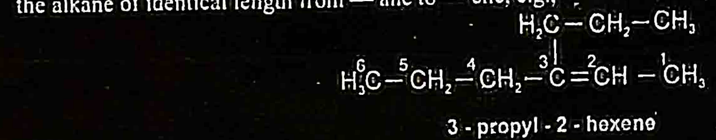
(i)	4- Methylpentane $CH_3-CH_2-CH_2-CH(CH_3)-CH_3$ **Correct name:** 2–Methylpentane	(ii)	3,5,5 - Trimethylhexane $CH_3-CH_2-CH(CH_3)-CH_2-C(CH_3)_2-CH_3$ **Correct name:** 2,2,4 – Trimethylhexane
(iii)	2-Methyl –3- ethylbutane $CH_3-CH(CH_3)-CH(CH_2)-CH_3$ **Correct name:** 2,3 – Dimethylpentane		

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Nomenclature of Alkenes

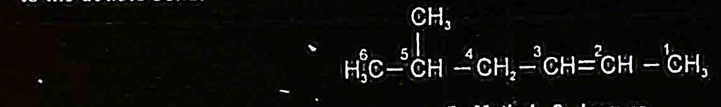
The IUPAC rules for naming alkenes are similar in many respects to those for naming alkanes.

1. Select the longest continuous chain that contains the C = C as the parent chain. Change the ending of the name of the alkane of identical length from — ane to — ene, e.g.,



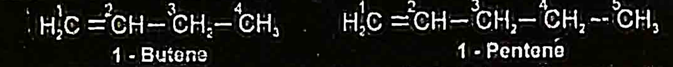
3 - propyl - 2 - hexene

2. Number the chain so as to include both carbon atoms of the double bond. Numbering begins from the end nearer to the double bond.



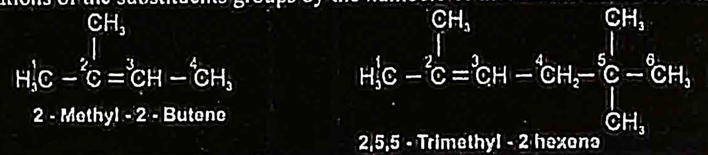
5 - Methyl - 2 - hexene

3. Designate the location of the double bond by using the number of the first atom of the double bond as a prefix.



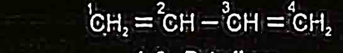
1 - Butene 1 - Pentene

4. Indicate the locations of the substituents groups by the numbers of the carbon atoms to which they are attached.



2 - Methyl - 2 - Butene 2,5,5 - Trimethyl - 2 hexene

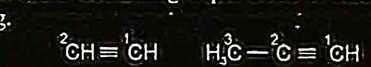
5. If the parent chain contains more than one double bonds, they are alkadienes for two, alkatrienes for three and so on.



1, 3 - Butadiene

Nomenclature of Alkynes

1. The largest continuous carbon chain containing triple bond is selected. The name of the identical alkane is changed from ane to —yne. e.g.



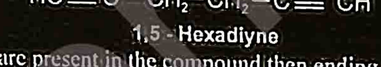
Ethyne Propyne

2. The position of triple bond is shown by numbering the alkyne, so that minimum number is assigned to the triple bond.



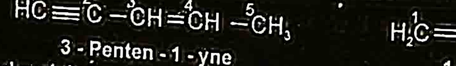
1 - Butyne 5 - Methyl - 1 - hexyne

3. If a hydrocarbon contains more than one triple bonds, it is named as alkadiyne and triyne etc, depending on the number of triple bonds.



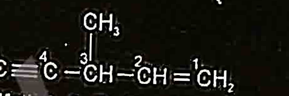
1,5 - Hexadiyne

4. If both double and triple bonds are present in the compound then ending enyne is given to the root.
(a) Lowest possible number is assigned to a double or a triple bond irrespective of whether ene or yne gets the lower number.



3 - Penten - 1 - yne 1 - Penten - 3 - yne

(b) In case a double and a triple bond are present at identical positions, the double bond is given the lower number.

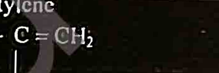
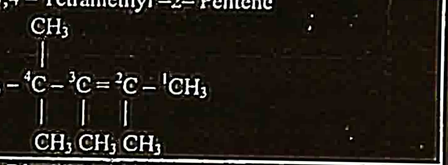
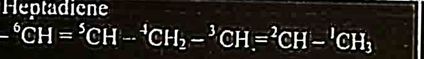
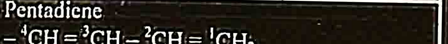
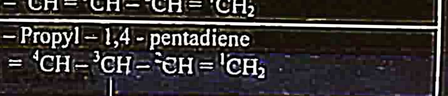
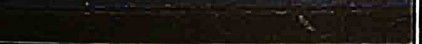
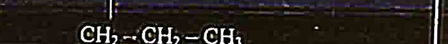
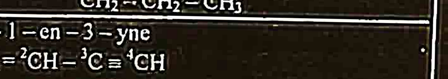


3 - Methyl - 1 - Penten - 4 - yne

Q11. (a) Write structural formulas for each of the following compounds.

(i) Isobutylene (ii) 2,3,4,4 - Tetramethyl - 2 - pentene
(iii) 2,5 - Heptadiene (iv) 4,5 - Dimethyl - 2 - hexene
(v) Vinylacetylene (vi) 1,3-pentadiene
(vii) 1-Butyne (viii) 3-n – propyl -1, 4-pentadiene
(ix) Vinyl bromide (x) But – 1 – en- 3 - yne
(xi) 4-Methyl-2pentyne (xii) iso- pentane

Ans. (a) Structural Formulas

(i) Isobutylene 	(ii) 2,3,4,4 – Tetramethyl –2– Pentene 
(iii) 2, 5 – Heptadiene 	(iv) 4,5 – Dimethyl – 2 – Hexene 
(v) Vinylacetylene 	(vi) 1,3 – Pentadiene 
(vii) 1 - Butyne 	(viii) 3 – n – Propyl – 1,4 - pentadiene 
(ix) Vinylbromide 	(x) But – 1 – en – 3 – yne 
(xi) 4- Methyl – 2 – pentyne 	(xii) Iso-Pentane 

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(b) Name the following compounds by IUPAC system.

(i) $H_3C - CH = CH(CH_2)_2CH_3$

(ii) $(CH_3)_2C = CH_2$

(iii) $CH_3 - CH_2 - CH_2 - C = CH_2$ with $CH(CH_3)_2$ as branch

(iv) $CH_2 = CH - CH = CH_2$

(v) $CH_2 = C - CH_2CH_2CH_3$ with C_2H_5 as branch

(vi) $CH \equiv C - CH_3$

(vii) $CH_3 - C \equiv C - CH_3$

(viii) $CH_2 = CH - C \equiv C - CH = CH_2$

(ix) $CH \equiv C - CH = CH - C \equiv CH$

(x) $CH_2 = CH - C \equiv CH$

Ans. IUPAC Names

(i) $H_3C - CH = CH - CH_2 - CH_2 - CH_3$ 2 – Hexene	(ii) $CH_3 - C(CH_3) = CH_2$ 2 – Methyl – 1 – propene
(iii) $CH_3 - CH_2 - CH_2 - C(CH(CH_3)_2) = CH_2$ 2 – Isopropyl – 1 – pentene	(iv) $CH_2 = CH - CH = CH_2$ 1,3 – Butadiene
(v) $CH_2 = C(C_2H_5) - CH_2CH_2CH_3$ 2 – Ethyl –1– pentene	(vi) $CH \equiv C - CH_3$ Propyne
(vii) $CH_3 - C \equiv C - CH_3$ 2-Butyne	(viii) $CH_2 = CH - C \equiv C - CH = CH_2$ 1,5 – Hexadien –3 – yne
(ix) $CH \equiv C - CH = CH - C \equiv CH$ 3-Hexene –1,5 - diyne	(x) $CH_2 = CH - C \equiv CH$ 1-Buten –3 – yne

ALKANES OR PARAFFINS

- Alkanes are the simplest organic compounds made up of carbon and hydrogen only.
- They have a general formula of C_nH_{2n+2}.
- In these compounds the four valencies of carbon atoms are satisfied by single bonds to either other carbon atoms or hydrogen atom.
- They are known as **Saturated Hydrocarbons.** Methane (CH_4) is the simplest member of this family.
- Each carbon atom in alkane is sp^3 hybridized and has a tetrahedral geometry.

Q.9(a) Outline the methods available for the preparation of alkanes.

General Methods of Preparations

(1) Hydrogenation of Unsaturated Hydrocarbons

(Sabatier-Sendern's Reaction)

The addition of hydrogen in alkenes or alkynes in the presence of nickel at 200-300°C yields alkanes is called hydrogenation.

Examples

$$R - CH = CH_2 + H_2 \xrightarrow[200 - 300\ ^oC]{Ni} R - CH_2 - CH_3$$

Alkene → Alkane

$$CH_2 = CH_2 + H_2 \xrightarrow[200 - 300\ ^oC]{Ni} CH_3 - CH_3$$

Ethene → Ethane

Catalysts

The hydrogenation can also be carried out with platinum or palladium at room temperature but they are expensive than nickel.

Industrial Importance

The method is of industrial importance. Production of vegetable ghee by the catalytic hydrogenation of vegetable oil (unsaturated fatty acids) is an example of the application of this method on industrial scale.

(2) From Alkyl Halides

(i) By reduction

An alkane is produced when an alkyl halide reacts with zinc in the presence of an aqueous acid.

$$\underset{\text{Alkyl halide}}{R - X} + Zn + H^+ + X^- \longrightarrow \underset{\text{Alkane}}{R - H} + ZnX_2$$

$$\underset{\text{Methyl Iodide}}{CH_3 - I} + Zn + H^+ + I^- \longrightarrow \underset{\text{Methane}}{CH_4} + ZnI_2$$

$$CH_3 - CH_2 - \underset{\underset{\text{2 - Bromobutane}}{Br}}{CH} - CH_3 + Zn + H^+ + Br^- \longrightarrow \underset{\text{n – Butane}}{CH_3 - CH_2 - CH_2 - CH_3} + ZnBr_2$$

Frankland Reaction

$R-X+Zn+R-X \rightarrow ZnX_2+R-R$

- CH_4 Cannot he prepared by this method.

(ii) Hydrogenolysis

Alkanes can also be prepared from alkyl halides using palladium-charcoal as a catalyst. The method is known as Hydrogenolysis (hydrogenation accompanied by bond cleavage).

$$R - X + H_2 \xrightarrow[\Delta]{Pd/C} R - H + H - X$$

Hydrogenation	Hydrogenolysis
• Addition of H_2	• Substitution of H_2
• Cleavage of π bond	• Cleavage of σ bond
• Catalysts are Ni, Pt or Pd	• Catalysts is Pd/C
• $R-CH=CH_2+H_2 \xrightarrow[200-300^oC]{Ni} R-CH_2-CH_3$	• $R-X+H_2 \xrightarrow[\Delta]{Pd/C} R-H+HX$

(3) Decarboxylation of Monocarboxylic Acids

(i) When sodium salts of fatty acids are heated with soda-lime (prepared by soaking quick lime (CaO) with caustic soda solution and drying the product). They eliminate a molecule of CO_2 to form alkanes.

$$\underset{\text{Sod. salt of an acid}}{R - \overset{O}{\overset{\|}{C}} - \bar{O}\overset{+}{Na}} + NaOH \xrightarrow[\Delta]{CaO} R - H + Na_2CO_3$$

$$\underset{\text{Sod. Propionate}}{H_3C - CH_2 - \overset{O}{\overset{\|}{C}} - \bar{O}\overset{+}{Na}} + NaOH \xrightarrow[\Delta]{CaO} \underset{\text{Ethane}}{H_3C - CH_3} + Na_2CO_3$$

(ii) Kolbe's Electrolytic Method

When a concentrated solution of sodium or potassium salt of a mono carboxylic acid is electrolysed, an alkane is produced. This method is only suitable for the preparation of symmetrical alkanes i.e. those of the type R—R. Methane cannot be prepared by this method

$$2RCOO^-Na^+ + 2H_2O \xrightarrow{Electrolysis} R - R + 2CO_2 + 2NaOH + H_2$$

Mechanism

It is known to involve the following mechanism.

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When potassium salt of acetic acid is electrolysed, acetate ion migrates towards the anode gives up one electron to produce acetate free radical ($CH_3COO^{\bullet}$), which decomposes to give a methyl free radical ($^{\bullet}CH_3$) and CO_2. Two such methyl radicals combine to give ethane.

Ionization of salt

$$2H_3C-\overset{O}{\overset{\|}{C}}-O^-K^+ \rightleftharpoons 2H_3C-\overset{O}{\overset{\|}{C}}-O^- + 2K^+$$

Reactions

At anode

$$2H_3C-\overset{O}{\overset{\|}{C}}-O^- \xrightarrow{\text{Electrolysis}} 2H_3C-\overset{O}{\overset{\|}{C}}-{}^{\bullet}O + 2e^-$$

$$2H_3C-\overset{O}{\overset{\|}{C}}-{}^{\bullet}O \longrightarrow 2\,{}^{\bullet}CH_3 + 2CO_2$$

$$^{\bullet}CH_3 + {}^{\bullet}CH_3 \longrightarrow \underset{\text{Ethane}}{H_3C-CH_3}$$

Q. How would you convert Ethanoic acid into Ethane?

At cathode

$$2H_2O + 2e^- \longrightarrow 2OH^- + H_2$$

$$2K^+ + 2OH^- \longrightarrow 2KOH$$

This reaction has limited synthetic applications as it forms a number of side products.

(4) From Carbonyl Compounds (Aldehydes or Ketones)

The carbonyl groups of aldehydes or ketones are reduced to methyl or methylene group respectively by either **Clemmensen or Wolf-Kishner's reduction.** In the former reaction a ketone is reduced to an alkane using zinc amalgam and hydrochloric acid whereas in the latter an aldehyde is reduced to alkane with hydrazine in the presence of KOH.

Clemmensen Reduction

$$\underset{\text{Acetone}}{H_3C-\overset{O}{\overset{\|}{C}}-CH_3} + 4[H] \xrightarrow{Zn\text{-}Hg/HCl} \underset{\text{Propane}}{H_3C-CH_2-CH_3} + H_2O$$

Wolf – Kishner's Reduction



$$H_3C-\overset{O}{\overset{\|}{C}}-H + 4[H] \xrightarrow[200^\circ C]{N_2H_4/KOH} H_3C-CH_3 + H_2O$$

In clemmensen reduction, Zn–Hg/HCl and in Wolf–Kishner's reduction N_2H_4/KOH is used to generate nascent hydrogen. Both these methods reduce carbonyl compounds (aldehyde & ketone) into alkanes.

(5) From Grignard Reagents

Alkyl halides react in anhydrous ether with magnesium to form alkyl magnesium halides, known as Grignard Reagent. They decompose on treatment with water or dilute acid to give alkanes. e.g.,



$$\overset{\delta-}{CH_3}\overset{\delta+}{MgBr} + \overset{\delta+}{H}-\overset{\delta-}{OH} \xrightarrow[H^+]{\text{ether}} CH_4 + Mg(Br)(OH)$$

$$H_3\overset{\delta-}{C}-\overset{\delta-}{CH_2}-\overset{\delta+}{MgBr} + \overset{\delta+}{H}-\overset{\delta-}{OH} \xrightarrow{H^+} H_3C-CH_3 + Mg(Br)(OH)$$

Grignard reagents on treating with water, alcohol and ammonia, produce alkanes.

Physical Properties

(i) Physical State:

- C_1 to C_4 (methane, ethane, propane, butane) are colourless and odourless gases.
- C_5 to C_{17} (pentane to heptadecane) are colourless, odourless liquids.
- The higher members from C_{18} onwards are waxy solids which are also colourless and odourless.

(ii) Solubility:

Alkanes are non-polar or very weakly polar and are insoluble in polar solvents like water, but soluble in non-polar solvents like benzene, ether, carbon tetra chloride, etc.

(iii) Physical constants:

Their physical constants like boiling points, melting points, density, etc increase with the increase in number of carbon atoms. Solubility decreases with increase in molecular mass.

The boiling point increases by 20 to 30°C for addition of each CH_2 group to the molecule.

The boiling points of alkanes having branched chain structures are lower than their isomeric normal chain alkanes, e.g., n-butane has a higher boiling point – 0.5°C than isobutane(-11.7°C).

- **The effect of branching on the boiling point of alkane:**

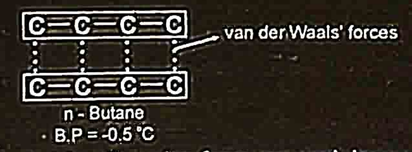
The boiling points of alkanes having branched chain structures are lower than their isomeric normal chain alkanes.

Q. Why the boiling point of straight chain hydrocarbons is greater then their isomeric branch chain hydrocarbons?

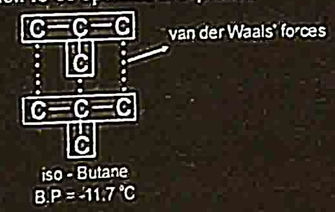
Explanation:-

As the boiling point of a molecule depends upon the strength of intermolecular forces.

- In n-butane the London dispersion forces are strong because the molecules are close to each other and the area of interaction between the two molecules is large. So London dispersion force is operating at four places.



Whereas, in iso-butane the London dispersion forces are weak because the distance between molecules increases and the area of interaction decreases due to branching Hence packing of molecules is not so tight and London dispersion force operates at 3 places.



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(iv) **Melting points:**

The melting points of alkanes also increase with the increase in molecular mass but this increase is not so regular.

Q8. (a) Explain why alkanes are less reactive than alkenes?

Reactivity of Alkanes

The alkanes or paraffins (Latin: parum = little, affins = affinity) under ordinary condition are inert towards acids, alkalis, oxidizing and reducing agents. However, under suitable conditions, alkanes do undergo two types of reactions.

(i) Substitution Reactions

(ii) Thermal and Catalytic Reactions

These reactions take place at high temperature or on absorption of light energy through the formation of highly reactive free radicals.

Q. Why alkanes are called paraffins? Or Alkanes are least reactive organic compounds. Justify

Ans **(i) Non – polar nature:**

The unreactivity of alkanes under normal conditions may be explained on the basis of the non-polarity of the bonds forming them. The eletronegativity values of carbon (2.5) and hydrogen (2.1) do not differ appreciably and the bonding electrons between C-H and C-C are equally shared making them almost non-polar. In view of this, the ionic reagents such as acids, alkalies, oxidizing agents, etc find no reaction site in the alkane molecules to which they could be attached.

(ii) Inertness of σ-bond:

The unreactivity of alkanes can also be explained on the basis of inertness of a σ-bond. In a σ-bond the electrons are very tightly held between the nuclei which makes it a very stable bond. A lot of energy is required to break it. Moreover, the electrons present in a σ-bond can neither attack on any electrophile nor a nucleophile can attack on them. Both these facts make alkanes less reactive.

Reactions of Alkanes

1. Combustion

"Burning of an alkane in presence of oxygen is known as **Combustion.**"

Complete combustion of an alkane yields CO_2, H_2O and heat. The amount of heat evolved when one mole of a hydrocarbon is burnt to CO_2 and H_2O is called heat of combustion.

Example

$$CH_4 + 2O_2 \xrightarrow{\text{flame}} CO_2 + 2H_2O + 891\ kJmol^{-1}$$

Although the reaction is highly exothermic, it requires very high temperature to initiate it, e.g. by a flame or a spark.

Combustion is the major reaction occurring in the internal combustion engines of automobiles. A compressed mixture of alkanes and air burns smoothly in the internal combustion engine and increases its efficiency.

2. Oxidation

Oxidation of methane under different conditions gives different products.

(i) Incomplete oxidation

Incomplete oxidation occurs in a limited supply of oxygen or air and results in the formation of CO and carbon black.

$$3CH_4(g) + 4O_2(g) \xrightarrow{\text{Flame}} 2CO(g) + 6H_2O(g) + C(s)$$

(ii) Catalytic Oxidation

Lower alkanes when burnt in the presence of metallic catalysts, at high temperature and pressure, results in the formation of useful products.

$$CH_4 + [O] \xrightarrow[400^\circ C/200atm]{Cu} \underset{\text{Methyl alcohol}}{H_3C-OH}$$

$$H_3C-OH + [O] \xrightarrow[400^\circ C/200atm]{Cu} HCHO + H_2O$$

$$\underset{\text{Formaldehyde}}{HCHO} + [O] \xrightarrow[400^\circ C/200atm]{Cu} \underset{\text{Formic acid}}{HCOOH}$$

$$HCOOH + [O] \xrightarrow[400^\circ C/200atm]{Cu} CO_2 + H_2O$$

Conversion

Q. How would you convert ethane into acetic acid?

Uses

Catalytic oxidation of alkanes is used industrially to prepare higher fatty acids used in soap and vegetable oil industries.

3. Nitration

"It is a substitution reactions of alkanes in which a hydrogen atom of an alkane is replaced by nitro group ($-NO_2$)."

Alkanes undergo vapour-phase nitration under drastic condition (at 400-500°C) to give nitroalkanes.

Example

$$CH_4 + HONO_2 \xrightarrow{400^\circ C} \underset{\text{Nitromethane}}{CH_3NO_2} + H_2O$$

Uses

Nitroalkanes generally find use as fuels, solvent, and in organic synthesis.

MCQ's

What product will be formed by the nitration of propane:

(a) Nitro methane

(b) Nitro ethane

(c) Nitro propane

(d) all of these

Q10. (b) Explain free radical mechanism for the reaction of chlorine with methane in the presence of sunlight.

4. Halogenation

"The successive replacement of hydrogen atoms of an alkane by halogen atom in the presence of sunlight or UV light or at high temperature is called halogenation."

The order of reactivity of halogens is $F_2 > Cl_2 > Br_2 > I_2$.

- Reaction of alkanes with fluorine is highly violent and results in a mixture of carbon, fluorinated alkanes and hydrofluoric acid.
- With chlorine and bromine, alkanes give substituted products at moderate rate.
- Iodine does not substitute directly because the reaction is too slow and reversible.
- Extent of halogenation depends upon the amount of halogen used.

Free radical mechanism

Halogenation is believed to proceed through free radical mechanism. It involves the following three steps.

Step I $Cl-Cl \xrightarrow{hr} Cl^{\bullet} + Cl^{\bullet}$ (Initiation)

Step II

$$H_3C-H + Cl^{\bullet} \xrightarrow{hr} \underset{\text{Methyl free radical}}{CH_3^{\bullet}} + HCl$$

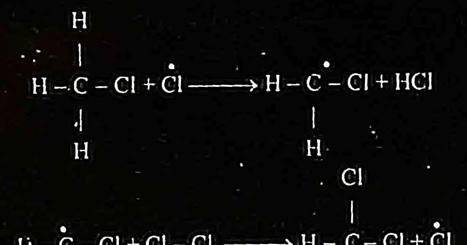
$$CH_3^{\bullet} + Cl-Cl \xrightarrow{hr} CH_3-Cl + Cl^{\bullet}$$

(Propagation)

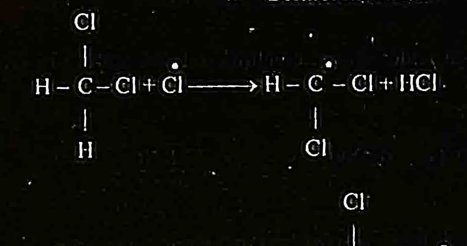
Step III $CH_3^{\bullet} + Cl^{\bullet} \longrightarrow \underset{\text{Methyl chloride}}{CH_3-Cl}$ (Termination)

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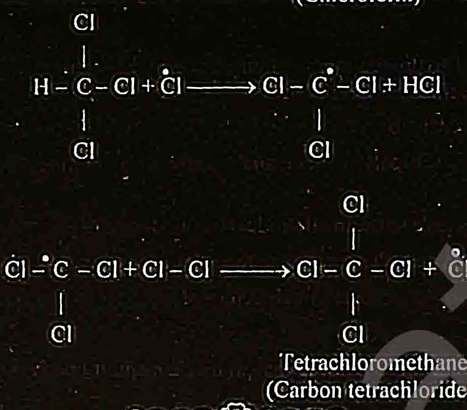
By repetition of step II, a mixture of halogen substituted products are obtained. The reaction is not synthetically so important.



Dichloromethane



Trichloromethane
(Chloroform)



Tetrachloromethane
(Carbon tetrachloride)

Q21. (c) Mention some important uses of methane.

Uses of Methane

Methane is used:

(i) as a fuel and as an illuminating gas.
(ii) for the preparation of methylchloride, methylene chloride, chloroform and carbon tetrachloride.
(iii) for the industrial prepartion of methyl alcohol, formaldehyde and hydrogen cyanide.
(iv) for the preparation of carbon black used in paints, printing inks and automobile tyres.
(v) is used to manufacture urea fertilizer.

ALKENES

- Alkenes have two hydrogen atoms less than the corresponding saturated hydrocarbons.
- They are also known as Olefins (derived from Latin word olefiant meaning oil forming) because lower members form oily products on treatment with chlorine or bromine.
- The simplest olefin is C_2H_4, ethene.
- Alkene having one double bond are known as mono-enes with general formula C_nH_{2n}.
- Alkenes containing two double bonds are called dienes.

Dienes having general formula C_nH_{2n-2}

Q12. (a) Describe different methods for the preparation of alkenes. How would you establish that ethylene contains a double bond?

General Methods of Preparation

1. Dehydrohalogenation of Alkyl Halides

Alkyl halides on heating with alcoholic potassium hydroxide undergo dehydrohalogenation i.e. elimination of a halogen atom together with a hydrogen atom from adjacent carbon atoms.

$$R-\underset{X}{CH_2}-CH_2 \xrightarrow{\text{Alc. KOH}} R-CH=CH_2 + KX + H_2O$$

$$\underset{H\ \ Br}{H_2C-CH_2} + KOH \xrightarrow{\text{Alcohol}} \underset{\text{Ethene}}{H_2C=CH_2} + KBr + H_2O$$

$$H_3C-CH_2-CH_2-Br + KOH \xrightarrow{\text{Alcohol}} H_3C-CH=CH_2 + KBr + H_2O$$

2. Dehydration of Alcohols

Alcohols when dehydrated in the presence of a catalyst give alkene. The best procedure is to pass vapours of alcohol over heated alumina.

$$\underset{\text{Alcohol}}{R-CH_2-\underset{OH}{CH_2}} \xrightarrow[340\text{-}450^\circ C]{Al_2O_3} \underset{\text{Alkene}}{R-CH=CH_2} + H_2O$$

P_4O_{10}, (conc) H_2SO_4 and H_3PO_4 are also used for dehydration. The ease of dehydration of various alcohols is in the order.

Ter. alcohol > Sec. alcohol > Pri.alcohol

Thus

$$\underset{\text{Primary Alcohol}}{R-CH_2-\underset{OH}{CH_2}} \xrightarrow[140\text{-}170^\circ C]{75\%\ H_2SO_4} R-CH=CH_2 + H_2O$$

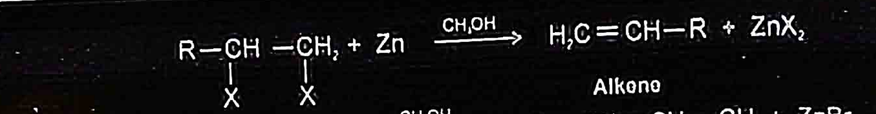
$$\underset{\text{Secondary Alcohol}}{R-CH_2-\underset{OH}{CH}-CH_3} \xrightarrow[100^\circ C]{60\%\ H_2SO_4} R-CH=CH-CH_3 + H_2O$$

$$\underset{\text{Tertiary Alcohol}}{R-\underset{CH_3}{\overset{CH_3}{C}}-OH} \xrightarrow[85^\circ C]{20\%\ H_2SO_4} R-\underset{CH_3}{C}=CH_2 + H_2O$$

3. Dehalogenation of Vicinal Dihalides

Vicinal dihalides have two halogens on adjacent carbon atoms. Dehalogenation occurs when dihalide is treated with Zinc dust in an anhydrous solvent like methanol or acetic acid.

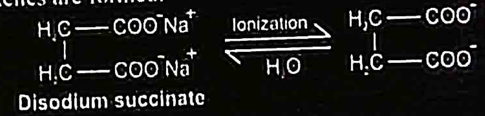
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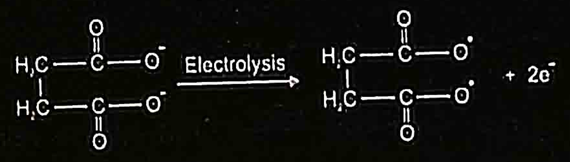
4. Electrolysis of Salts of Dicarboxylic acid

(Kolbe's Electrolytic Method)

When sodium or potassium salts of the dicarboxylic acid like succinic acid are subjected to electrolysis in an aqueous solution, alkenes are formed.



At anode



At cathode

$2H_2O + 2e^- \longrightarrow 2OH^- + H_2$

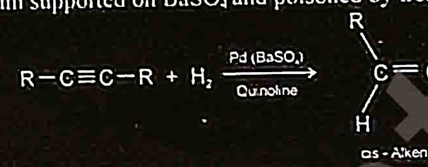
$2Na^+ + 2OH^- \longrightarrow 2NaOH$

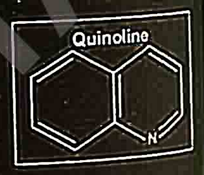
Q. Write down the mechanism for preparation of 2-Butene from Kolbe's electrolytic method.

5. Partial Hydrogenation of Alkynes

(i) Formation of cis-alkene

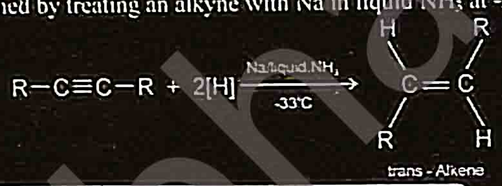
Controlled hydrogenation of alkynes with hydrogen gas in an equimolar ratio over heated catalysts, gives alkenes. The catalyst is finely divided palladium supported on $BaSO_4$ and poisoned by treatment with quinoline (Lindlar's catalyst).





(ii) Formation of trans-alkene

A trans alkene can be obtained by treating an alkyne with Na in liquid NH_3 at -33°C.



Q. How would you convert 2-Butyne into (i) Cis 2-Butene (ii) Trans 2-Butene.

Q. What is Lindlar's catalyst? How it ensure the partial hydrogenation of alkynes?

Physical Properties

1. First three members i.e. ethene, propene and butene are gases at room temperature while C_5 to C_{15} are liquids and the higher members are solids.
2. They are insoluble in water but soluble in alcohol.
3. They have characteristic smell and burn with luminous flame.
4. Unlike alkanes, they show weakly polar properties because of sp^2 hybridization.

Q. Alkenes are highly reactive hydrocarbons. Justify.

Ans **Reactivity of a π-bond:**

In the formation of a π-bond, the partially filled p-orbitals overlap in a parallel fashion. The probability of finding electron is thus away from the line joining the two nuclei. Due to this reason π-electrons are less firmly held between the nuclei. A π-bond is, therefore, a weak bond as compared to a σ-bond. During a reaction it breaks comparatively easily rendering alkenes as reactive group of compounds. Moreover, the loosely held π-electrons are more exposed to attack by the electrophilic reagents. Alkenes, therefore, undergo electrophilic reactions very easily.

Reactions of Alkenes

A. Addition Reactions

Q.27 (b) Give the general mechanism of electrophilic addition reactions of alkenes

Ans

Mechanism of Electrophilic Addition Reactions of Alkene

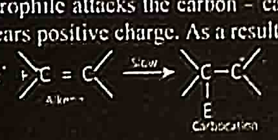
It involves the following steps:

The reagent E – Nu ionizes to give an electrophile and nucleophile.

$$E - Nu \longrightarrow E^+ + :Nu$$

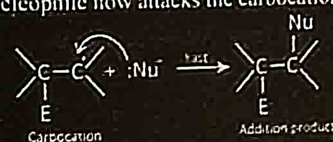
Step 1:

The electrophile attacks the carbon – carbon double bond and forms a covalent bond with one carbon and other carbon bears positive charge. As a result a carbocation is formed.



Step 2:

The nucleophile now attacks the carbocation to form an addition product.



Since the reaction is initiated by addition of electrophile, so it is called electrophilic addition reaction.

1. Addition of Hydrogen (Hydrogenation)

Definition

Hydrogenation is a process in which a molecule of hydrogen is added to an alkene in the presence of a catalyst and at moderate pressure (1-5 atm.) to give a saturated compound. The process is known as **Catalytic Hydrogenation.**

Heat of hydrogenation

It is a highly exothermic process and the amount of heat evolved when one mole of an alkene is hydrogenated is called **Heat of Hydrogenation.** The heat of hydrogenation of most alkenes is about 120kJmole^{-1} for each double bond present in a molecule.

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Catalyst

The catalysts employed are Pt, Pd and Raney nickel.

Applications

Catalytic hydrogenation of alkenes is used in the laboratory as well as in industry.

- **In industry,** it is used for the manufacture of vegetable ghee from vegetable oils.
- **In the laboratory,** it is used as a synthetic method as well as an analytical tool, as the reaction is generally quantitative.

Q. What is Raney nickel? How it increases the rate of reaction?

Ans **Raney Nickel:**

Raney nickel is a spongy form of nickel. It has porous surface.

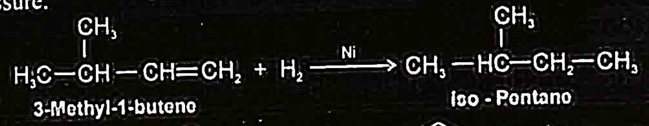
Preparation:

It is prepared by treating a Ni — Al alloy with caustic soda.

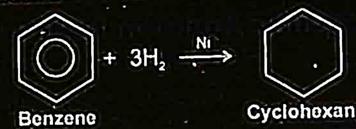
$$Ni - Al + NaOH + H_2O \longrightarrow Ni + NaAlO_2 + 3/2H_2$$

Reactivity of Raney Nickel:

Large surface area of Raney Nickel due to its spongy form makes it an effective catalyst as compare to simple metal. Thus it increases the rate of reaction. Most alkenes are hydrogenated over Raney nickel at about 100°C and upto 3-atmospheres pressure.



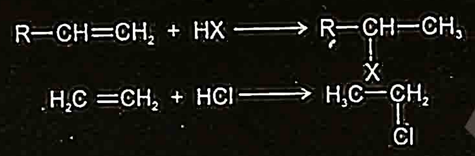
3-Methyl-1-butene — Iso - Pentane



Benzene — Cyclohexane

2. Addition of Hydrogen Halides

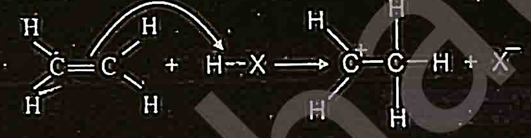
Alkenes react with dry gaseous hydrogen halides to form alkyl halides. The order of reactivity of halogen acids is HI > HBr> HCl.



Mechanism

The addition of a hydrogen halide to an alkene takes place in two steps. Alkene accepts the proton of hydrogen halide to form a carbocation.

(i) Formation of carbocation



The carbocation then reacts with the halide ion.

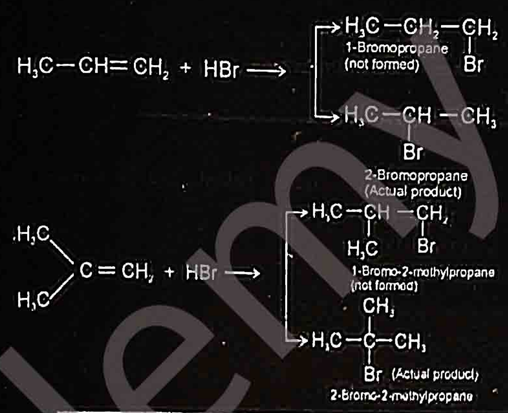
(ii) Attack of nucleophile



Markownikov's Rule

The addition of hydrogen halide over an unsymmetrical alkene is done by Markownikov's Rule. The rule states that.

"In the addition of an unsymmetrical reagent to an unsymmetrical alkene, the negative part of the adding reagent goes to that carbon, constituting the double bond, which has least number of hydrogen atoms."



MCQ's

Which of the following product is obtained when propene is treated with HBr in the presence of peroxide.

(a) 1–Bromopropane
(b) 2–Bromopropane
(c) 1–Bromopropene
(d) 1,2-Dibromopropane

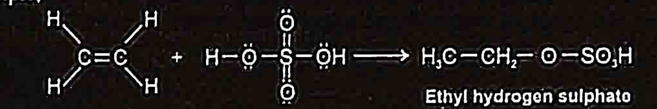
HINT:

Kharasch method (anti Markownikov's rule)

Q14. (a) How may ethene be converted into ethyl alcohol?

Ans. Addition of Sulphuric Acid (hydration)

When alkenes are treated with cold concentrated sulphuric acid, they are dissolved because they form alkyl hydrogen sulphate. For example,



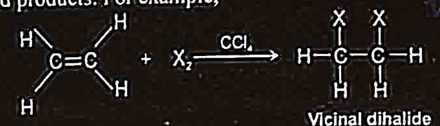
Ethyl hydrogen sulphate

These alkylhydrogen sulphates on boiling with water decompose to give corresponding alcohols. The overall reaction involves the addition of water to an alkene and it is, therefore, called hydration reaction.

$$H_3C - CH_2 - O - SO_3H + H_2O \xrightarrow{100^\circ C} H_3C - CH_2 - OH + H_2SO_4$$

4. Addition of Halogens

The alkenes on treatment with halogen in an inert solvent like carbon tetrachloride at room temperature give vicinal dihalides or 1,2 dihalogenated products. For example,



Vicinal dihalide

Br_2 and Cl_2 are effective electrophilic reagents. Fluorine is too reactive to control the reaction. Iodine does not react.

Mechanism

Formation of bromonium ion

(a) A bromine molecule becomes polarized as it approaches the alkene. This polarized bromine molecule transfers a positive bromine atom to the alkene resulting in the formation of a bromonium ion.

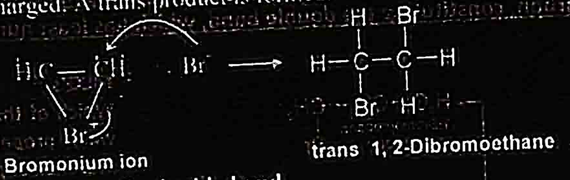


Bromonium ion

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Attack of nucleophile

(b) The nucleophilic bromide ion then attacks on the carbon of the bromonium ion to form vicinal dibromide and the colour of bromine is discharged. A trans product is formed.

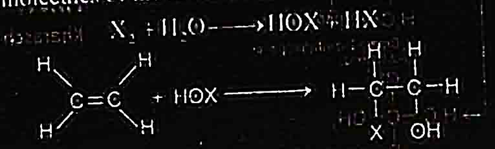


This test is used for the detection of a double bond.

5. Addition of Hypohalous acid (HOX)

If the halogenation of an alkene is carried out in an aqueous solution, haloalcohol is formed called a Halohydrin. In this reaction, molecules of the solvent become reactants too.

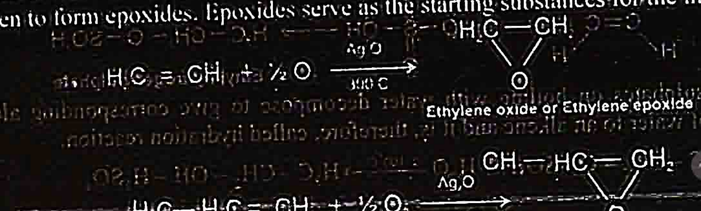
$$X_2 + H_2O \longrightarrow HOX + HX$$



B. OXIDATION REACTIONS

1. Addition of Oxygen

Alkenes when mixed with oxygen or air and passed over a silver oxide catalyst at high temperature and pressure, add an atom of oxygen to form epoxides. Epoxides serve as the starting substances for the industrial production of glycols.



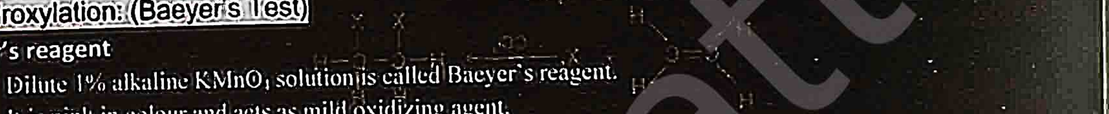
2. Hydroxylation: (Baeyer's Test)

Baeyer's reagent

- Dilute 1% alkaline $KMnO_4$ solution is called Baeyer's reagent.
- It is pink in colour and acts as mild oxidizing agent.

Reaction

When alkenes are treated with mild oxidizing reagents like dilute (1%) alkaline $KMnO_4$ solution (Baeyer's Reagent) at low temperature, hydroxylation of double bond occurs resulting in the formation of dihydroxy compounds known as vicinal glycols. The pink colour of $KMnO_4$ solution is discharged during the reaction.



It is also a test for the presence of unsaturation in the molecules.

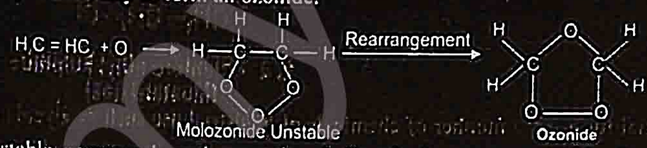
3. Combustion

Alkenes burn in air with luminous flame and produce CO_2 and H_2O vapours. Ethene forms a highly explosive mixture with air or oxygen.

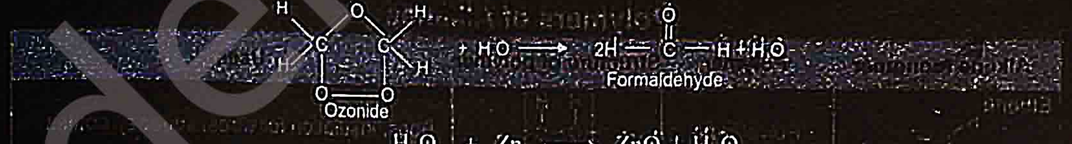
$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O + \text{heat}$$

4. Ozonolysis

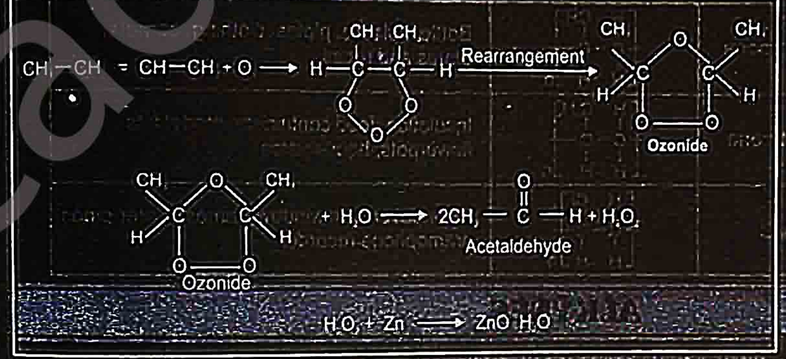
Ozone (O_3) is a highly reactive allotropic form of oxygen. It reacts vigorously with alkenes to form unstable molozonide. It rearranges spontaneously to form an ozonide.



Ozonides are unstable compounds and are reduced directly by treatment with zinc and H_2O. The reduction produces carbonyl compounds (aldehydes or ketones).



$$H_2O_2 + Zn \longrightarrow ZnO + H_2O$$



MCQ's

What will be the position of double bond when in alkene acetaldehyde and propanone are formed on ozonolysis?

(a) C_1
(b) C_2
(c) C_3
(d) C_4

Ozonolysis is used to locate the position of double bond in an alkene.

C. Polymerization

In this process small organic molecules (monomers) combine together to form larger molecules known as Polymers. Ethene at 400°C and 100 atm pressure, polymerize to polythene or polyethylene.

$$n\ CH_2 = CH_2 \xrightarrow[\text{100 atm pressure}\ \text{traces of } O_2\ (0.1\%)]{400^\circ C} \left[CH_2 - CH_2\right]_n$$

Polyethylene

A good quality polythene is obtained, when ethene is polymerized in the presence of aluminium triethyl $Al(C_2H_5)_3$ and titanium tetrachloride catalysts ($TiCl_4$).

Uses of Ethene

Ethene is used:

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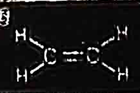
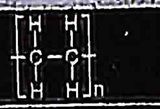
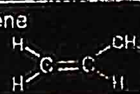
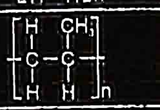
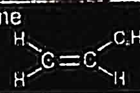
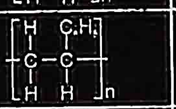
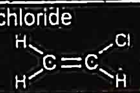
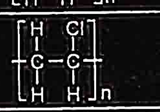
(i) for the manufacture of polythene, a plastic material used for making toys, cables, bags, boxes, etc.
(ii) for artificial ripening of the fruits,
(iii) as a general anaesthetic,
(iv) for preparing 'Mustard gas' a chemical used in World War I. The name comes from its mustard like odour. It is not a gas, but a high boiling liquid that is dispersed as a mist of tiny droplets. It is a powerful vesicant i.e., causes blisters.

$$2CH_2 = CH_2 + S_2Cl_2 \longrightarrow S(CH_2-CH_2-Cl)_2 + S$$

2, 2' - Dichloro ethyl sulphide (Mustard gas)

(v) as a starting material for a large number of chemicals of industrial use such as glycols (antifreeze), ethyl halide, ethyl alcohol, etc.

Polymers of Alkenes

Alkene monomer	Polymer	Structure of polymer	Uses
Ethene 	Polyethene		Bags, insulation for wires, squeezy bottles
Propene 	Polypropene		Bottles, plastic, plates, clothing, carpets, crates and ropes
Styrene 	Polystyrene		Insulation, food containers, model kits flowerpots, housewares
Vinylchloride 	PVC		Floor coverings, window frames, water pipes, gramophone recorder

ALKYNES

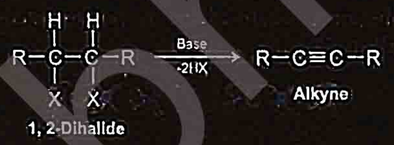
- Unsaturated hydrocarbons which contain a triple bond are called Alkynes.
- They have the general molecular formula C_nH_{2n-2} and contain two hydrogen atoms less than the corresponding alkenes.
- The first member of the Alkyne series has the formula C_2H_2 and is known as ethyne or acetylene.

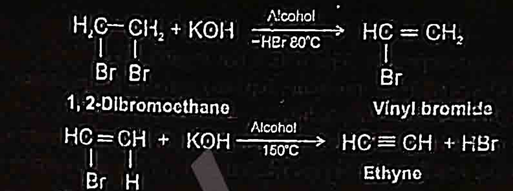
Q21. (a) Describe methods for the preparation of Ethyne.

General Methods of Preparation

1. Dehydrohalogenation of Vicinal Dihalides

Vicinal dihalide on treatment with a strong base eliminates two molecules of hydrogen halides from two adjacent carbons to give an alkyne.

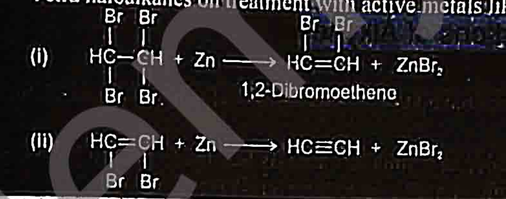




The second molecule of hydrogen halide is removed with great difficulty and requires drastic conditions.

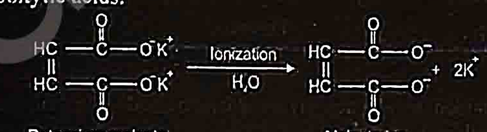
2. Dehalogenation of Tetrahalides

Tetra haloalkanes on treatment with active metals like Zn, Mg, etc. form alkynes.

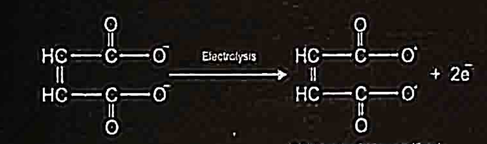


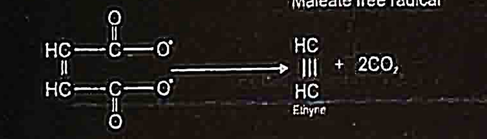
3. Electrolysis of Salts of Unsaturated Dicarboxylic Acids

Kolbe's electrolytic method involves electrolysis of aqueous solution of Na or K salts of unsaturated dicarboxylic acids.



At anode:-





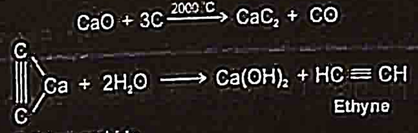
At Cathode:-

$$2H_2O + 2e^- \longrightarrow 2OH^-$$
$$2K^+ + 2OH^- \longrightarrow 2KOH$$

Industrial Preparation of Ethyne

On industrial scale ethyne is prepared by the reaction of calcium carbide (CaC_2) with water. Calcium carbide is prepared by heating lime (CaO) and coke (C) at a very high temperature in an electric furnace.

$$CaO + 3C \xrightarrow{2000\,^\circ C} CaC_2 + CO$$



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Physical Characteristics

1. They are colourless, odourless, except acetylene which has a garlic like odour.
2. The first three members are gases (ethyne, propyne, butyne) at room temperature. The next eight members (C_5 - C_{12}) are liquids and higher members are solids.
3. The melting points, boiling points and densities increase gradually with the increase in molecular masses.
4. They are nonpolar and dissolve readily in solvents like ether, benzene and carbon tetrachloride.

Reactivity of Alkynes

In alkynes, the carbon atoms are held together by a triple bond, a σ – bond and two π-bonds. The electron density between the carbon atoms is very high which draws atoms very close to each other. Electrons in a triple bond are, therefore, less exposed and thus less reactive towards electrophilic reagents.

Reactions of Alkynes

A. Addition Reactions:

Alkynes undergo addition reactions like alkenes but add two molecules of the reagent instead of one.

1. Addition of Hydrogen:

Alkynes react with hydrogen gas in the presence of a suitable catalysts like finely divided Ni, Pt, or Pd. Initially alkenes are formed which then take up another molecule of hydrogen to form an alkane.

$$HC\equiv CH + H_2 \xrightarrow[\text{heat}]{Ni} H_2C=CH_2$$

Ethyne — Ethene

$$CH_2=CH_2 + H_2 \xrightarrow[\text{heat}]{Ni} H_3C-CH_3$$

Ethene — Ethane

2. Addition of Halogens

One or two molecules of halogens can be added to alkynes giving dihalides and tetra halides respectively. Chlorine and bromine add readily while iodine reacts rather slowly.

$$HC\equiv CH + Cl_2 \xrightarrow{CCl_4} \underset{Cl}{\overset{H}{}}C=C\underset{H}{\overset{Cl}{}}$$

Ethyne — 1, 2 - Dichloroethene

$$\underset{Cl}{\overset{H}{}}C=C\underset{H}{\overset{Cl}{}} + Cl_2 \xrightarrow{CCl_4} H-\underset{Cl}{\overset{Cl}{C}}-\underset{Cl}{\overset{Cl}{C}}-H$$

1, 1, 2, 2 - Tetrachloroethane

3. Addition of Halogen Acids

Alkynes react with hydrogen chloride and hydrogen bromide to form dihaloalkanes. The reaction occurs in accordance with Markownikov's rule.

$$HC\equiv CH + H-Br \longrightarrow H_2C=\underset{Br}{CH}$$

Ethyne — Vinyl bromide

$$H_2C=\underset{Br}{CH} + H-Br \xrightarrow[\text{addition}]{\text{Markownikov's}} H_2C-\underset{Br}{\overset{Br}{CH}}$$

1, 1 - Dibromoethane

4. Addition or Water

Water adds to alkynes in the presence of mercuric sulphate dissolved in sulphuric acid at 75°C. The reaction is important industrially. For example.

$$HC\equiv CH + H-OH \xrightarrow[75^\circ C]{HgSO_4} \underset{\text{Vinyl alcohol}}{H_2C=\underset{O-H}{CH}}$$

Vinyl alcohol is an unstable enol. The enol has the hydroxy group attached to a doubly bonded carbon atom and isomerises to acetaldehyde.

$$H_2C=\underset{O-H}{CH} \longrightarrow \underset{\text{Acetaldehyde}}{H_3C-\overset{O}{\overset{\|}{C}}-H}$$

All other alkynes give ketones.

$$H_3C-C\equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} H_3C-\overset{O-H}{\overset{|}{C}}=CH_2 \longrightarrow \underset{\text{Acetone (Ketone)}}{H_3C-\overset{O}{\overset{\|}{C}}-CH_3}$$

5. Addition of Ammonia and Hydrogen Cyanide:

NH_3 and HCN react with ethyne in the presence of suitable catalysts, to give nitriles.

$$CH\equiv CH + NH_3 \xrightarrow[300^\circ C]{Al_2O_3} \underset{\text{Acetonitrile}}{H_3C-C\equiv N} + H_2$$

$$CH\equiv CH + HCN \xrightarrow{Cu\,Cl\,/NH_4Cl} \underset{\text{Acrylonitrile}}{CH_2=CH-CN}$$

B. Oxidation Reactions

1. Ethyne on oxidation with strong alkaline $KMnO_4$ gives glyoxal.

$$HC\equiv CH + 2H_2O + 2[O] \xrightarrow{KMnO_4} \underset{OH}{\overset{O-H}{HC}}-\underset{OH}{\overset{O-H}{CH}} \xrightarrow{-2H_2O} \underset{\text{Glyoxal}}{\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H}$$

ethyne — Glyoxal

$$\underset{\text{Glyoxal}}{HC(=O)-CH(=O)} \xrightarrow[KMnO_4]{2[O]} \underset{\text{Oxalic acid}}{\overset{O}{\overset{\|}{C}}(-OH)-\overset{O}{\overset{\|}{C}}(-OH)} \quad \text{or } (COOH)_2$$

2. Combustion

Alkynes when burnt in air or oxygen produce heat and evolves CO_2 and H_2O. The reaction is highly exothermic for acetylene and the resulting oxyacetylene flame is used for welding and cutting of metals

$$2HC\equiv CH + 5O_2 \longrightarrow 4CO_2 + 2H_2O + \text{heat}$$

C. Polymerization

Alkynes polymerize to give linear or cyclic compounds depending upon the temperature and catalyst used. However, these polymers are different from the polymers of the alkenes as they are usually low molecular weight polymers.

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1. Conversion of Acetylene to Divinyl Acetylene

When acetylene is passed through an acidic solution of cuprous chloride and ammonium chloride and then allowed to stand for several hours at room temperature, vinyl acetylene and divinyl acetylene are obtained.

$$HC\equiv CH + HC\equiv CH \xrightarrow{Cu_2Cl_2,NH_4Cl} \underset{\text{Vinyl acetylene (1-Buten-3-yne)}}{H_2C=CH-C\equiv CH}$$

$$H_2C=CH-C\equiv CH + HC\equiv CH \xrightarrow{Cu_2Cl_2,NH_4Cl} \underset{\text{Divinyl acetylene (1,5-Hexadien-3-yne)}}{H_2C=CH-C\equiv C-CH=CH_2}$$

Formation of chloroprene

If HCl is added to vinyl acetylene, chloroprene is obtained which readily polymerize to neoprene, used as synthetic rubber.

$$\underset{\text{Vinyl acetylene}}{H_2C=CH-C\equiv CH} + \text{conc. HCl} \xrightarrow{Cu_2Cl_2,NH_4Cl} \underset{\text{Chloroprene}}{H_2C=CH-\overset{Cl}{\overset{|}{C}}=CH_2}$$

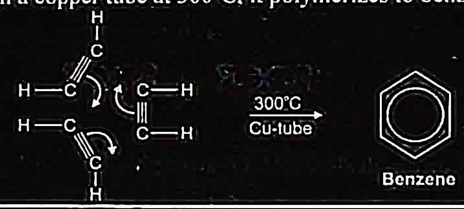
Neoprene
$-(H_2C-CH=C-CH_2)_n-$
Cl
• First man made rubber

Formation of neoprene

$$\text{Chloroprene} \xrightarrow{\text{Polymerization}} \text{Neoprene (synthetic rubber)}$$

2. Conversion of Acetylene to Benzene

When acetylene is passed through a copper tube at 300°C, it polymerizes to benzene.



Benzene

Q23.(b) Write a note on the acidity of ethyne.

Acidic Nature of Alkynes

In ethyne and other terminal alkynes like propyne, the hydrogen atom is bonded to the carbon atom with sp-s overlap. An sp hybrid orbital has 50% s character in it and renders the carbon atom more electronegative than sp^2 and sp^3 hybridized carbons. As a result, the sp hybridized carbon atom of a terminal alkyne pulls the electrons more strongly making the attached hydrogen atom slightly acidic.

$$H^{\delta+}-C^{\delta-}\equiv C^{\delta-}-H^{\delta+}$$

(i) When 1-Alkyne or ethyne is treated with sodamide in liquid ammonia or passed over molten sodium, alkynides or acetylides are obtained.

$$R-C\equiv CH + NaNH_2 \xrightarrow{\text{liq } NH_3} R-C\equiv C^-Na^+ + NH_3$$

$$HC\equiv CH + 2Na \longrightarrow \underset{\text{Sodium acetylide}}{Na^+C^-\equiv C^-Na^+} + H_2$$

Sodium acetylide is a very valuable reagent for chemical synthesis and is essentially ionic in nature.

(ii) Acetylides of copper and silver are obtained by passing acetylene in the ammoniacal solution of cuprous chloride and silver nitrate respectively.

$$HC\equiv CH + Cu_2Cl_2 + 2NH_4OH \longrightarrow \underset{\text{Dicopperacetylide (Reddish brown ppt.)}}{CuC\equiv CCu} + 2NH_4Cl + 2H_2O$$

$$HC\equiv CH + 2AgNO_3 + 2NH_4OH \longrightarrow \underset{\text{Disilver acetylide (white ppt.)}}{AgC\equiv CAg} + 2NH_4NO_3 + 2H_2O$$

Silver and copper acetylides react with acids to regenerate alkynes.

$$AgC\equiv CAg + H_2SO_4\ (dil.) \longrightarrow HC\equiv CH + Ag_2SO_4$$

$$AgC\equiv CAg + 2HNO_3\ (dil.) \longrightarrow HC\equiv CH + 2AgNO_3$$

These alkynides are used for the preparation, purification, separation, and identification of alkynes.

Q. Distinguish between:
(i) 1-Butyne and 2-Butyne
(ii) Ethyne and Ethene

Uses of Ethyne

Ethyne is used:

(i) in oxyacetylene torch which is in turn used for welding and cutting metals.
(ii) for the preparation of alcohols, acetic acid and acetaldehyde.
(iii) for the manufacture of polymers like PVC, polyvinyl acetate, polyvinyl ethers, orlon and neoprene rubber.
(iv) to prepare acetylene tetrachloride a solvent for varnishes, resins, and rubber.
(v) for ripening of fruits.

Q.22 How you could distinguish ethane, ethane and ethyne from one another by means of chemical reactions?

Distinguish Between Alkane, Alkene and Alkyne

Distinguish Test	Alkane (Ethane)	Alkene (Ethene)	Alkyne (Ethyne)
Br_2/CCl_4	No reaction	Decolourises $C_2H_4 + Br_2 \longrightarrow C_2H_4Br_2$	Decolourises $C_2H_2 + Br_2 \longrightarrow C_2H_2Br_2$
Baeyer's reagent (Alk. $KMnO_4$)	No reaction	Decolourises $CH_2=CH_2 + H_2O + [O] \longrightarrow \underset{CH_2OH}{\overset{CH_2OH}{\overset{\vert}{\vert}}}$	• Do not react with dilute alkaline aqueous solution of $KMnO_4$ • Alkynes are oxidized by strong alkaline solution of $KMnO_4$ to give oxalic acid. $CH\equiv CH + 4[O] \longrightarrow (COOH)_2$
Ammoniacal Cu_2Cl_2	No reaction	No reaction	Reddish brown ppt. $\underset{CH}{\overset{CH}{\vert\vert\vert}} + Cu_2Cl_2 + 2NH_4OH \longrightarrow \underset{CCu}{\overset{CCu}{\vert\vert\vert}} + 2NH_4Cl + 2H_2O$
Tollen's Reagent (Ammoniacal $AgNO_3$)	No reaction	No reaction	White ppt. $\underset{CH}{\overset{CH}{\vert\vert\vert}} + 2AgNO_3 + 2NH_4OH \longrightarrow \underset{CAg}{\overset{CAg}{\vert\vert\vert}} + 2NH_4NO_3 + 2H_2O$

Q24. (a) Compare the reactivity of ethane, ethene and ethyne.

Comparison of Reactivities of Alkanes, Alkenes and Alkynes

The general decreasing reactivity order of alkanes, alkenes and alkynes is as follows:

Alkenes > Alkynes > Alkanes

It has already been explained that a π–bond in alkenes is not only weak but its electrons are more exposed to an attack by an electrophilic reagent. Both these facts make the alkenes a very reactive class of compounds. Alkynes although contain two π–bonds are less reactive than alkenes towards electrophilic regents. This is because the bond distance between the two triple bonded carbon atoms is very short and hence the π–electrons are not available to be attacked by electrophilic reagents. Alkynes are, however, more reactive than alkenes towards nucleophilic reagents.

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KEY POINTS

1. Hydrocarbons are made up of carbon and hydrogen only. Saturated hydrocarbons are called alkanes. They do not contain functional groups.
2. Alkanes react with halogens by a radical mechanism to give haloalkanes. The mechanism consists of three steps, initiation, propagation and termination.
3. Alkenes are unsaturated hydrocarbons with at least one C = C. The double bond is composed of a ____ and a ____ bond. Carbon atoms in alkenes are sp^2 hybridized.
4. Alkenes are very reactive compounds. They undergo electrophilic reactions very easily.
5. Addition of unsymmetrical reagent to an unsymmetrical alkene takes place in accordance with the Markownikov's rule.
6. Alkenes can be very easily oxidized with cold $KMnO_4$ solution. O_3 or ozone. With ozone both the bonds between carbon atoms are cleaved.
7. Hydrocarbons containing a triple bond are known as alkynes or acetylenes.
8. Alkynes undergo addition reactions and two molecules of a reagent are added in it.
9. Ethyne and other terminal alkynes contain a weakly acidic hydrogen and they react with ammoniacal cuprous chloride and ammoniacal silver nitrate to give acetylides.
10. The decreasing reactivity order of alkanes, alkenes and alkynes are as follows:

Alkenes > Alkynes > Alkynes

SOLVED OBJECTIVE EXERCISE

Q1. Fill in the blanks:

(i) Ozone reacts with ethene to form _____.
(ii) Lindlar's catalyst is used for _____ of alkynes.
(iii) Divinyl acetylene is a _____ acetylene.
(iv) Vicinal dihalides have two halogens on _____ carbon atoms.
(v) Ethyne is acidic in character because of _____ hybridization.
(vi) Halohydrins are formed due to addition of _____ in ethene.
(vii) Ethylene glycol is produced when _____ reacts with cold alkaline $KMnO_4$ solution.
(viii) Mustard gas is a high boiling _____.
(ix) Ethyne has _____ like odour.
(x) Ethyne is obtained by the reaction of _____ with calcium carbide.

Answer Key.

(i)	Ozonide	(ii)	Partial hydrogenation
(iii)	Polymer of	(iv)	Adjacent
(v)	sp.	(vi)	Hypohalous acid
(vii)	Ethene	(viii)	Liquid
(ix)	Garlic	(x)	Water

Q2. Indicate True or false:

(i) Addition of HX to unsymmetrical alkanes takes place according to Markownikov's rule.
(ii) Methane reacts with bromine water and its colour is discharged.
(iii) Mustard gas is a blistering agent.
(iv) Methane is also called marsh gas.
(v) Ethyne is a saturated compound.
(vi) Baeyer's reagent is used to locate a double bond in an alkene.
(vii) Alkanes usually undergo substitution reactions.
(viii) Benzene is a polymer of ethene.
(ix) Acrylonitrile can be obtained from ethyne.
(x) Ethyne is more reactive towards electrophilic reagents than ethene.

Answer Key.

(i)	False	(ii)	False	(iii)	True	(iv)	True	(v)	False
(vi)	True	(vii)	True	(viii)	False	(ix)	True	(x)	False

Q3. Multiple Choice Questions. Encircle the correct answer:

(i) Preparation of vegetable ghee involves
(a) Halogenation (b) Hydrogenation (c) Hydroxylation (d) Dehydrogenation

(ii) Formula of chloroform is:
(a) CH_3Cl (b) CCl_4 (c) CH_2Cl_2 (d) $CHCl_3$

(iii) The presence of a double bond in a compound is the sign of:
(a) Saturation (b) Unsaturation (c) Substitution (d) None

(iv) Vinyl acetylene combines with HCl to form:
(a) Polyacetylene (b) Benzene (c) Chloroprene (d) Divinyl acetylene

(v) The addition of unsymmetrical reagent to an unsymmetrical alkene is in accordance with the rule.
(a) Hund's rule (b) Markownikov's rule (c) Pauli's Exclusion principle (d) Aufbau principle

(vi) Synthetic rubber is made by polymerization of:
(a) Chloroform (b) Acetylene (c) Divinylacetylene (d) Chloroprene

(vii) β,β'- dichloroethyl sulphide is commonly known as:
(a) Mustard gas (b) Laughing gas (c) Phosgene gas (d) Bio-gas

(viii) When methane reacts with Cl_2 in the presence of diffused light, the products obtained are:
(a) Chloroform only (b) Carbon tetrachloride only
(c) Chloromethane and dichloromethane (d) Mixture of a, b, c

(ix) Which one of the following gases is used for artificial ripening of fruits:
(a) Ethene (b) Ethyne (c) Methane (d) Propane

Solved Exercise MCQ's

Q.No.	Answer	Reason
(i).	(b) Hydrogenation	Vegetable Oil + H_2 $\xrightarrow[200°C]{Ni}$ Vegetable ghee
(ii).	(d) $CHCl_3$	Trichloromethane ($CHCl_3$) is also called chloroform.
(iii).	(b) Unsaturation	It means any molecule can add into it. $CH_2=CH_2$ is unsaturated compound.
(iv).	(c) Chloroprene	$CH_2 = CH - C \equiv CH + HCl \rightarrow CH_2 = CH - C = CH_2$ (Cl)
(v).	(b) Markownikov's rule	Negative part of attacking reagent goes to that carbon containing double bond and has least number of hydrogen atoms.
(vi).	(d) Chloroprene	Chloroprene $\xrightarrow{Polymerization}$ Neoprene (Synthetic rubber)
(vii).	(a) Mustard gas	It is not a gas but a high boiling liquid.
(viii).	(d) Mixture of a, b, c	First form CH_3Cl then CH_2Cl_2, $CHCl_3$ and CCl_4 respectively.
(ix).	(a) Ethene	Ethyne is used for ripening of fruits.

SOLVED ANSWERS TO EXERCISE

Q9. (b) How will you bring about the following conversions?

(i) Methane to ethane.
(ii) Ethane to methane.
(iii) Acetic acid to ethane.
(iv) Methane to nitromethane.

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Ans. (b) (i) Methane → Ethane

$$CH_4 + Cl_2 \xrightarrow{\text{Sunlight}} \underset{\text{Methylchloride}}{CH_3 - Cl} + HCl$$

$$CH_3 - Cl + 2Na + Cl - CH_3 \xrightarrow{\text{Ether}} \underset{\text{Ethane}}{CH_3 - CH_3} + 2NaCl$$

(ii) Ethane → Methane

$$CH_3 - CH_3 + [O] \xrightarrow[400^\circ C/200atm]{Cu} CH_3 - CH_2 - OH$$

$$CH_3 - CH_2 - OH + CH_3MgI \xrightarrow{\text{Ether}} \underset{\text{Methane}}{CH_4} + \underset{\text{Ethoxymagnesium iodide}}{Mg(OCH_2 - CH_3)I}$$

(Ethanol)

(iii) Acetic acid → ethane:

$$CH_3COOH + 6HI \xrightarrow{P} \underset{\text{Ethane}}{CH_3 - CH_3} + 2H_2O + 3I_2$$

(iv) Methane → nitromethane:

$$CH_4 + HONO_2 \xrightarrow{450^\circ C} \underset{\text{Nitromethane}}{CH_3 - NO_2} + H_2O$$

Q12. (b) Give structure formulas of the alkenes expected to form by the dehydrohalogenation of the following compounds with a strong base:
(i) 1-Chloropentane (ii) 2-Chloro-3-methylbutane (iii) 1-Chloro-2, 2-dimethyl propane

Ans. (b) (i) 1– Chloropentane

$$\overset{5}{C}H_3 - \overset{4}{C}H_2 - \overset{3}{C}H_2 - \overset{2}{C}H_2 - \overset{1}{C}H_2 + KOH \xrightarrow[80^\circ C]{\text{Alcohol}} KCl + H_2O + \overset{5}{C}H_3 - \overset{4}{C}H_2 - \overset{3}{C}H_2 - \overset{2}{C}H = \overset{1}{C}H_2$$

(1-Chloro: $\overset{1}{C}H_2$–Cl; 1-Pentene)

(ii) 2- Chloro -3- Methylbutane

$$CH_3 - CH(CH_3) - CH(Cl) - CH_3 + KOH \xrightarrow[80^\circ C]{\text{Alcohol}} CH_3 - C(CH_3) = CH - CH_3 + KCl + H_2O$$

2 – Methyl – 2 – butene

(iii) 1 – Chloro -2,2 – Dimethylpropane:

$$CH_3 - C(CH_3)_2 - CH_2 + KOH \xrightarrow[80^\circ C]{\text{Alcohol}} \text{No reaction}$$

Because β – H is not available

Q13. (a) Write down chemical equations for the preparation of propene from the compounds.
(i) $CH_3 - CH_2 - CH_2 - OH$ (ii) $CH_3 - C \equiv CH$ (iii) iso-Propyl chloride

Ans. (a)
(i) $CH_3 - CH_2 - CH_2 - OH$

$$CH_3 - CH_2 - CH_2 - OH \xrightarrow[140-170^\circ C]{75\%H_2SO_4} CH_3 - CH = CH_2 + H_2O$$

1 - propanol — Propene

(ii) $CH_3 - C \equiv CH$

$$CH_3 - C \equiv CH + H_2 \xrightarrow[\text{Quinoline}]{Pd(BaSO_4)} CH_3 - CH = CH_2$$

propyne — Propene

(iii) iso-Propylchloride

$$CH_3 - CH(Cl) - CH_3 + KOH \xrightarrow{\text{Alcohol}} KCl + H_2O + H_3C - CH = CH_2$$

Propene

Q13. (b) Write skeleton formula showing only the arrangement of carbon atoms for all the possible alkenes of the molecular formula C_5H_{10}.

Ans. (b) Possible alkenes of formula C_5H_{10}

(i) $\overset{5}{C}H_3 - \overset{4}{C}H_2 - \overset{3}{C}H_2 - \overset{2}{C}H = \overset{1}{C}H_2$ — 1 – Pentene

(ii) $\overset{5}{C}H_3 - \overset{4}{C}H_2 - \overset{3}{C}H = \overset{2}{C}H - \overset{1}{C}H_3$ — 2 – Pentene

(iii) $\overset{4}{C}H_3 - \overset{3}{C}H_2 - \overset{2}{C}(CH_3) = \overset{1}{C}H_2$ — 2 – Methyl -1- butene

(iv) $\overset{4}{C}H_3 - \overset{3}{C}H = \overset{2}{C}(CH_3) - \overset{1}{C}H_3$ — 2 – Methyl -2- butene

(v) $H_3C - C(H)(CH_3) - CH = CH_2$ — 3 – Methyl -1- butene

Q14. (b) Starting from ethene, outline the reactions for the preparation of following compounds.
(i) 1,2-Ethyl dibromide (ii) Ethyne
(iii) Ethane (iv) Ethylene glycol

Ans. (b)
(i) 1,2 – Ethyldibromide

$$CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4} \underset{\text{1,2 – Ethyldibromide}}{CH_2(Br) - CH_2(Br)}$$

Ethene

(ii) Ethyne

$$H_2C = CH_2 + Br_2 \xrightarrow{CCl_4} H_2C(Br) - CH_2(Br)$$

Ethene

$$H_2C(Br) - CH_2(Br) + 2KOH \xrightarrow[80^\circ C]{\text{Alcohol}} HC \equiv CH + 2KBr + 2H_2O$$

1,2 – Dibromoethane — Ethyne

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(iii) Ethane

$$H_2C = CH_2 + H_2 \xrightarrow{Ni} H_3C - CH_3$$

Ethene → Ethane

(iv) Ethylene glycol

$$3H_2C = CH_2 + 2KMnO_4 + 4H_2O \xrightarrow{Cold} 2MnO_2 + 2KOH + 3H_2C(OH) - CH_2(OH)$$

Ethylene glycol

Q14. (c) How will you bring about the following conversions:

(i) 1-Butene to 1-Butyne

(ii) 1-Propanol to $CH_3 - \underset{OH}{CH} - CH_2Cl$

Ans. (c)

(i) 1 – Butene to 1 – Butyne

- $H_3C - CH_2 - CH = CH_2 + Br_2 \xrightarrow{CCl_4} CH_3CH_2 - \underset{Br}{CH} - \underset{Br}{CH_2}$

  1 – Butene

- $CH_3 - CH_2 - \underset{Br}{CH} - \underset{Br}{CH_2} + 2KOH \xrightarrow[80°C]{Alcohol} 2KBr + 2H_2O + CH_3 - CH_2 - C \equiv CH$

  1 – Butyne

(ii) 1 Propanol to $CH_3 - \underset{OH}{CH} - CH_2Cl$

- $CH_3 - CH(OH) - CH_3 \xrightarrow[\text{Dehydration}]{Conc.\ H_2SO_4} CH_3 - CH = CH_2 + H_2O$

  1 – Propanol → Propene

- $CH_3 - CH = CH_2 + HOCl \rightarrow CH_3 - \underset{OH}{CH} - \underset{Cl}{CH_2}$

  Propene → 1 – Chloro – 2 – Propanol

Q.15. Show by means of chemical equations how the following cycle of changes may be affected.

Ethane ⟶ Ethene ⟶ Ethyne

Ans. Ethane ⟶ Ethene ⟶ Ethyne

(i) Ethane → Ethene

- $H_3C - CH_3 + Br_2 \xrightarrow{hv} H_3C - CH_2 - Br + HBr$

  Ethane → Ethylbromide

- $H_3C - CH_2 - Br + KOH \xrightarrow{Alcohol} H_2C = CH_2 + KBr + H_2O$

  Ethene

(ii) Ethene → Ethyne:

- $H_2C = CH_2 + Br_2 \xrightarrow{CCl_4} H_2C(Br) - CH_2(Br)$

  Ethene → 1,2 – Dibromoethane

- $H_2C(Br) - CH_2(Br) + 2KOH \xrightarrow[80°C]{Alcohol} 2KBr + 2H_2O + HC \equiv CH$

  → Ethyne

(iii) Ethyne to Ethane:

- $HC \equiv CH + H_2 \xrightarrow[200-300°C]{Ni} H_2C = CH_2$

  Ethyne → Ethene

- $H_2C = CH_2 + H_2 \xrightarrow[200-300°C]{Ni} H_3C - CH_3$

  Ethene → Ethane

Q16. Write down structural formulas for the products that are formed when 1-butene will react with the following reagents

(i) H_2, Pt (ii) Br_2 in CCl_4 (iii) Cold dil. $KMnO_4$\OH⁻
(iv) HBr (v) O_2 in the presence of Ag (vi) HOCl
(vii) dil. H_2SO_4

Ans.

(i) H_2, Pt:-

$$CH_3 - CH_2 - CH = CH_2 + H_2 \xrightarrow{Pt} CH_3 - CH_2 - CH_2 - CH_3$$

1 – Butene → n – Butane

(ii) Br_2 in CCl_4 :-

$$CH_3 - CH_2 - CH = CH_2 + Br_2 \xrightarrow{CCl_4} CH_3 - CH_2 - \underset{Br}{CH} - \underset{Br}{CH_2}$$

Butene → 1, 2– Dibromobutane

(iii) Cold dilute $KMnO_4$/OH⁻ :-

$$3CH_3 - CH_2 - CH = CH_2 + 2KMnO_4 + 4H_2O \xrightarrow{Cold} 3CH_3 - CH_2 - \underset{OH}{CH} - \underset{OH}{CH_2} + 2MnO_2 + 2KOH$$

1, 2 – Butanediol

(iv) HBr :-

$$CH_3 - CH_2 - CH = CH_2 + HBr \longrightarrow CH_3 - CH_2 - \underset{Br}{CH} - CH_3$$

2 – Bromobutane

(v) O_2 in the presence of Ag:-

$$H_2C - CH_2 - CH = CH_2 + \tfrac{1}{2}O_2 \xrightarrow[200°C]{Ag} CH_3 - CH_2 - \underset{\diagdown\ \diagup}{CH} - CH_2$$

O

Butylene epoxide

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(vi) HOCl :-

$CH_3 - CH_2 - CH = CH_2 + HOCl \longrightarrow CH_3 - CH_2 - \underset{OH}{CH} - \underset{Cl}{CH_2}$

1- Chloro – 2 – Hydroxy butane

(vii) Dilute H_2SO_4 :-

$CH_3 - CH_2 - CH = CH_2 + H - \ddot{O} - SO_3H \rightarrow CH_3 - CH_2 - \underset{OSO_3H}{CH} - CH_3$

2 – Butyl hydrogen sulphate

$CH_3 - CH_2 - \underset{OSO_3H}{CH} - CH_3 + H_2O \xrightarrow{100^\circ C} H_2SO_4 + CH_3 - CH_2 - \underset{OH}{CH} - CH_3$

2- Butanol

Q17. In the following reactions identify each lettered product.

(i) Ethyl alcohol $\xrightarrow{\text{conc. } H_2SO_4}$ A $\xrightarrow{Br_2}$ B $\xrightarrow[KOH]{\text{alcoholic}}$ C

(ii) Propene $\xrightarrow{Br_2}$ D $\xrightarrow[KOH]{\text{alcoholic}}$ E $\xrightarrow{HCN}$ F

Ans.

(i) Ethyl alcohol $\xrightarrow{\text{Conc. } H_2SO_4}$ A $\xrightarrow{Br_2}$ B $\xrightarrow[KOH]{\text{alcoholic}}$ C

- $CH_3 - CH_2 - OH \xrightarrow[140-170^\circ C]{75\% H_2SO_4} CH_2 = CH_2 + H_2O$

  Ethylalcohol — Ethene

- $CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4} \underset{Br}{CH_2} - \underset{Br}{CH_2}$

  Ethene — 1-2 Dibromoethane

- $CH_2 - CH_2 + 2KOH \xrightarrow[80^\circ C]{\text{Alcohol}} HC \equiv CH + 2KBr + 2H_2O$

  Br Br — Ethyne

  1, 2 – Dibromoethane

Hence

A = Ethene — B = 1, 2 – Dibromoethane

C = Ethyne

(ii) Propene $\xrightarrow{Br_2}$ D $\xrightarrow[KOH]{\text{Alcohol}}$ E $\xrightarrow{HCN}$ F

- $CH_3 - CH = CH_2 + Br_2 \xrightarrow{CCl_4} H_3C - \underset{Br}{\overset{H}{C}} - \underset{Br}{CH_2}$

  1 – 2 Dibromopropane

- $CH_3 - \underset{Br}{CH} - \underset{Br}{CH_2} + 2KOH \xrightarrow[KOH]{\text{Alcohle}} 2KBr + 2H_2O + CH_3 - C \equiv CH$

  Propyne

- $H_3C - C \equiv CH + HCN \xrightarrow[\Delta]{CuCl_2, NH_4Cl} H_3C - \underset{CN}{C} = CH_2$

  2- Cyanopropene

Hence

D = 1, 2 - Dibromopropane — E = Propyne

F = 2 Cyanopropene

Q18. After an ozonolysis experiment, the only product obtained was acetaldehyde, CH_3CHO. Can you guess the structural formula of this compound.

Ans. 2 – Butene

- $CH_3 - CH = CH - CH_3 + O_3 \longrightarrow CH_3 - \underset{O}{\overset{O}{CH}} - \underset{O}{\overset{O}{CH}} - CH_3$

  2 - Butene — Molozonide (unstable)

- $CH_3 - CH - CH - CH_3 \sim$ 

  Molozonide — Ozonide

-  $+ H_2O \longrightarrow 2CH_3 - \underset{O}{\overset{O}{C}} - H + H_2O_2$

  Ozonide — Acetaldehyde

$H_2O_2 + Zn \longrightarrow ZnO + H_2O$

Q19. (a) The addition of sulphuric acid to an alkene obeys Markownikov's rule. Predict the structures of the alcohols obtained by the addition of the acid to the following compounds.

(i) Propene

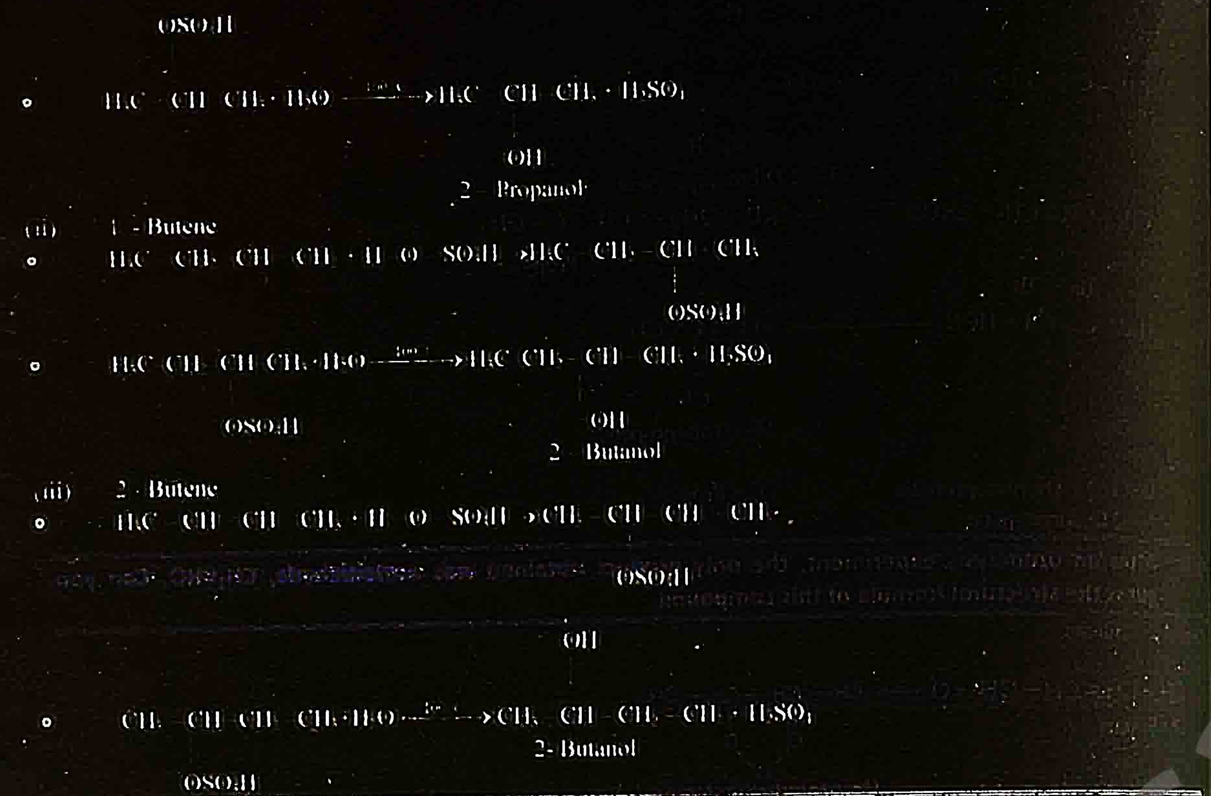
(ii) 1-Butene

(iii) 2-Butene

Ans. (i) Propene.

- $H_3C - CH = CH_2 + H - O - \underset{O}{\overset{O}{S}} - O - H \rightarrow H_3C - \underset{OSO_3H}{CH} - CH_3$

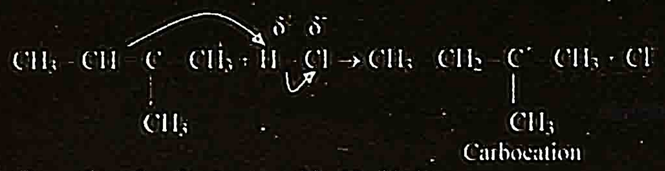
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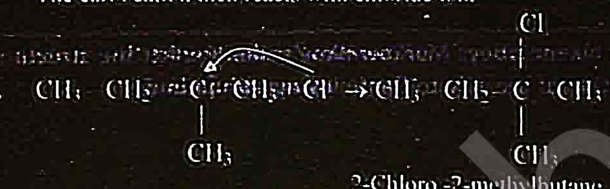
Q19. **(b) Predict the most likely product of the addition of hydrogen chloride to 2-methyl -2 butene. Explain the formation of this product.**

Ans. **(b)** The addition of hydrogen chloride to 2 – methyl -2 butene takes place in two steps.

(i) 2 - Methyl -2 butene accepts the proton of hydrogen chloride as follows:



(ii) The carbocation then reacts with chloride ion.



Q21. **(b) How does ethyne react with:**

(i) Hydrogen (ii) Halogen acid (iii) Alkaline $KMnO_4$
(iv) 10% H_2SO_4 in the presence of $HgSO_4$ (v) Ammonical cuprous chloride

(c) Mention some important uses of methane, ethene and ethyne.

Ans. **(b) How does ethyne react with**

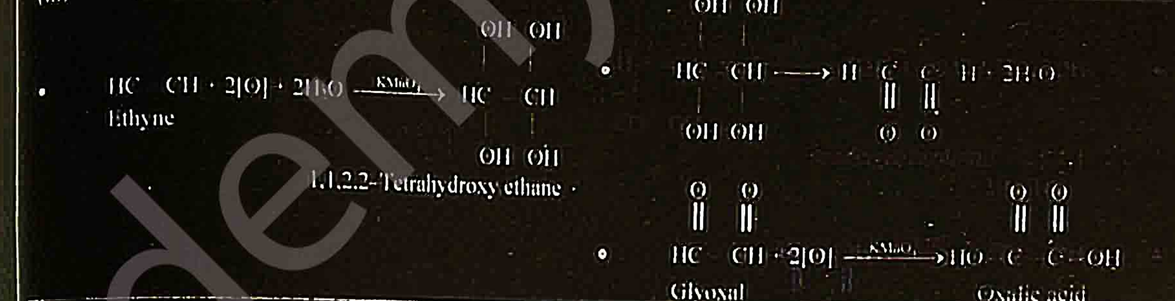
(i) Hydrogen



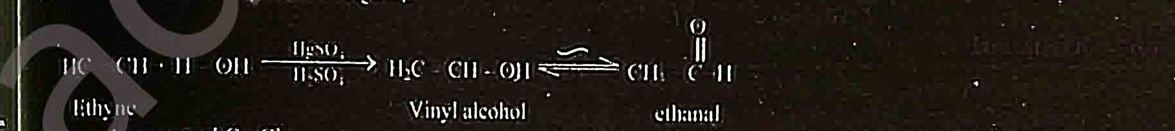
(ii) Halogen Acid:



(iii) Alkaline $KMnO_4$:



(iv) 10% H_2SO_4 in present of $HgSO_4$:



(v) Ammonical Cu_2Cl_2:

$HC \equiv CH + Cu_2Cl_2 + 2NH_4OH \rightarrow 2NH_4Cl + 2H_2O + CuC \equiv CCu$

Dicopper acetylide
(Reddish brown ppt)

Q23. **(a) How will you synthesize the following compounds starting from ethyne.**

(i) Acetaldehyde (ii) Benzene (iii) Chloroprene
(iv) Glyoxal (v) Oxalic acid (vi) Acrylonitrile
(vii) Ethane (viii) Methyl nitrile

(b) Write a note on the acidity of ethyne.

Ans. (a) (i) Acetaldehyde



(ii) Benzene



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(iii) Chloroprene

$$HC \equiv CH + HC \equiv CH \xrightarrow[\Delta]{Cu_2Cl_2, NH_4Cl} H_2C = CH - C \equiv CH$$

Vinyl acetylene

$$H_2C{=}CH{-}C{\equiv}CH + \text{Conc. } HCl \xrightarrow[\Delta]{Cu_2Cl_2/NH_4Cl} H_2C = CH - \underset{\displaystyle Cl}{\overset{\displaystyle |}{C}} = CH_2$$

Chloroprene

(iv) Glyoxal

$$HC \equiv CH + 2H_2O + 2[O] \xrightarrow{KMnO_4} \underset{\displaystyle HO}{\overset{\displaystyle HO}{\overset{\displaystyle |}{HC}}} - \underset{\displaystyle OH}{\overset{\displaystyle OH}{\overset{\displaystyle |}{CH}}}$$

1,1,2,2 - Tetrahydroxyethane

$$\underset{\displaystyle OH}{\overset{\displaystyle OH}{\overset{\displaystyle |}{HC}}} - \underset{\displaystyle OH}{\overset{\displaystyle OH}{\overset{\displaystyle |}{CH}}} \xrightarrow{-2H_2O} \underset{\displaystyle O}{\overset{\displaystyle O}{\overset{\displaystyle ||}{HC}}} - \underset{\displaystyle O}{\overset{\displaystyle O}{\overset{\displaystyle ||}{CH}}}$$

Glyoxal

(v) Oxalic acid

$$HC \equiv CH + 2[O] + 2H_2O \xrightarrow{KMnO_4} \underset{\displaystyle OH}{\overset{\displaystyle OH}{\overset{\displaystyle |}{HC}}} - \underset{\displaystyle OH}{\overset{\displaystyle OH}{\overset{\displaystyle |}{HC}}}$$

Ethyne — 1,1,2,2 – Tetrahydroxyethane

$$\underset{\displaystyle OH}{\overset{\displaystyle OH}{\overset{\displaystyle |}{HC}}} - \underset{\displaystyle OH}{\overset{\displaystyle OH}{\overset{\displaystyle |}{CH}}} \longrightarrow H - \underset{\displaystyle O}{\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}} - \underset{\displaystyle O}{\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}} - H + 2H_2O$$

$$\underset{\displaystyle O}{\overset{\displaystyle O}{\overset{\displaystyle ||}{HC}}} - \underset{\displaystyle O}{\overset{\displaystyle O}{\overset{\displaystyle ||}{CH}}} \xrightarrow[KMnO_4]{2[O]} HO - \underset{\displaystyle O}{\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}} - \underset{\displaystyle O}{\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}} - OH$$

Glyoxal — Oxalic acid

(vi) Acrylonitrile

$$HC \equiv CH + HCN \xrightarrow[\Delta]{NH_4Cl/Cu_2Cl_2} H_2C = CH - CN$$

Acrylonitrile

(vii) Ethane

$$HC \equiv CH + H_2 \xrightarrow[200-300^\circ C]{Ni} H_2C = CH_2$$

Ethene

$$H_2C = CH_2 + H_2 \xrightarrow[200-300^\circ C]{Ni} H_3C - CH_3$$

Ethene — Ethane

(viii) Methylnitrile

$$HC \equiv CH + NH_3 \xrightarrow[300^\circ C]{Al_2O_3} H_3C - C \equiv N + H_2$$

Methylnitrile

Q25. How does propyne react with the following reagents?
(a) $AgNO_3/NH_4OH$ (b) Cu_2Cl_2/NH_4OH (c) $H_2O/H_2SO_4, HgSO_4$.

Ans. (a) $AgNO_3$ / NH_4OH

(a) $H_3C - C \equiv CH + AgNO_3 + NH_4OH \rightarrow H_2O + NH_4NO_3 + H_3C - C \equiv C - Ag$

Propyne — Silver Propynide

(b) Cu_2Cl_2/ NH_4OH

$2H_3C - C \equiv CH + Cu_2Cl_2 + 2NH_4OH \rightarrow 2H_2O + 2NH_4Cl + 2CH_3C - C \equiv CCu$

Propyne — Copper Propynide

(c) H_2O / H_2SO_4, $HgSO_4$

$$H_3C - C \equiv CH + H - OH \xrightarrow[H_2SO_4]{HgSO_4} H_3C - \underset{\displaystyle OH}{\overset{\displaystyle |}{C}} = CH_2$$

Propyne

$$H_3C - C = CH_2 \rightleftharpoons CH_3 - \underset{\displaystyle O}{\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}} - CH_3$$

Acetone

Q26. A compound has a molecular formula C_4H_6. When it is treated with excess hydrogen in the presence of Ni-catalyst, a new compound C_4H_{10} is formed. When C_4H_6 is treated with ammonical silver nitrate, a white precipitate is formed. What is the structural formula of the given compound.

Ans. There are two compounds having molecular formula C_4H_6

(i) $CH_3 - CH_2 - C \equiv CH$

1 – Butyne

(ii) $CH_3 - C \equiv C - CH_3$

2 – Butyne

When both of them are treated with excess hydrogen in the Presence of Ni-catalyst, a new compound C_4H_{10} is formed.

(i) 1- Butyne

$$CH_3 - CH_2 - C \equiv C + H_2 \xrightarrow[\Delta]{Ni} CH_3 - CH_2 - CH = CH_2$$

1 – Butene

$$CH_3 - CH_2 - CH = CH_2 + H_2 \xrightarrow[\Delta]{Ni} CH_3 - CH_2 - CH_2 - CH_3$$

n – Butane

(ii) 2- Butyne

$$CH_3 - C \equiv C - CH_3 \xrightarrow[\Delta]{Ni} CH_3 - CH = CH - CH_3$$

2 – Butyne — 2-Butene

$$CH_3 - CH = CH - CH_3 + H_2 \xrightarrow[\Delta]{Ni} CH_3 - CH_2 - CH_2 - CH_3$$

n – Butane

However when C_4H_6 is treated with ammonical silver nitrate, a white precipitate is formed.

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(i) 1- Butyne

$CH_3-CH_2-C\equiv CH + AgNO_3 + NH_4OH \rightarrow NH_4NO_3 + H_2O + CH_3-CH_2-C\equiv CAg$

Silver Butynide

(ii) 2- Butyne

$CH_3-C\equiv C-CH_3 + AgNO_3 + NH_4OH \rightarrow$ No reaction

No reaction takes place as 2-Butyne contains no acidic hydrogen (hydrogen bonded with Sp-Hybridized carbon-atom)

Result:

Hence the given compound is 1- Butyne and its structural formula is:

$CH_3-CH_2-C\equiv CH$ (1-Butyne)

Q.27 Identify A and B

$$CH_3CH_2CH_2OH \xrightarrow{PCl_5} A \xrightarrow{Na/Ether} B$$

Ans. (a) $CH_3-CH_2-CH_2-OH \xrightarrow{PCl_5} A \xrightarrow{Na/Ether} B$

- $CH_3-CH_2-CH_2-OH + PCl_5 \longrightarrow CH_3-CH_2-CH_2-Cl + HCl + POCl_3$

Propylchloride

- $2CH_3-CH_2-CH_2-Cl + 2Na \xrightarrow[ether]{} CH_3-CH_2-CH_2-CH_2-CH_2-CH_3 + 2NaCl$

n-Hexane

Result: A = Propyl Chloride, B = n - Hexane

Previous Board Questions

1. Draw the structures of given compounds:
   (a) 4-Isopropyl Heptane (b) 3-Ethyl Pentane
2. Write down chemical equations for the preparation of Propene from the following compounds:
   (a) $CH_3-CH_2-CH_2-OH$ (b) $CH_3-C\equiv CH$
3. How does Ethyne react with
   (a) Ammonical Cuprous Chloride (b) Excess Cl_2 in CCl_4
4. What is meant by Polymerization? Give two different examples of Polymerization.
5. Give the mechanism of the electrophilic addition reactions of alkenes.
6. What is Baeyer's test? Give its use.
7. How Tollen's reagent can be used to distinguish between 1-butyne and 2-butyne?
8. Give reactions for preparation of followings from Ethene:
   (a) Ethylene glycol (b) Mustard gas
9. Write two general methods for the preparation of Ethyne.
10. What is hydroxylation of Alkenes? Give reaction.
11. Give chemical reactions for the preparation of oxalic acid from ethyne.
12. How a trans-alkene is obtained by the partial hydrogenation of alkynes?
13. Define Markownikov's rule. Give an example.
14. Write structural formula of (a) Vinylacetylene (b) But-1-en-3-yne
15. Write down the uses of ethyne.
16. Alkenes are more reactive than alkanes. Justify?
17. Why acetylene is acidic in character?
18. How will you distinguish between alkene and alkyne?
19. Why π - bond is more reactive than σ - bond ?
20. What is hydrogenolysis? Give an example.
21. What is Raney nickel and where is it used?

22. Write structural formula of the following compounds
    (a) Vinyl bromide (b) Iso-pentane
23. Describe two methods for the preparation of alkenes.
24. Why is ethane an important industrial chemical?
25. Give the correct IUPAC names of
    (a) Isopentane (b) Propylene
26. How will you prepare acetic acid from acetylene?
27. Justify that alkenes are more reactive then benzene.
28. How Benzene is obtained from acetylene?
29. Using ethyne as a starting material how would you get ethyl alcohol?
30. What is Lindlar's catalyst? Give its use.
31. How will you distinguish between ethane and ethyne?
32. What is Clemmensen's reduction?
33. Using ethyne as starting material, how would you get acetaldehyde and acetone?

For Answers STUDY
Scholar's CHEMISTRY (Objective) XII
AVAILABLE IN MARKET BY THE SAME AUTHORS

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CHAPTER 9

AROMATIC HYDROCARBONS

INTRODUCTION

Q.6 What is meant by the term aromatic?

Ans The term **aromatic** was derived from the Greek word **'aroma'** meaning **"fragrant"** (Pleasant odour) and was used in organic chemistry for a special class of compounds. These compounds have a low hydrogen to carbon ratio (or high carbon to hydrogen ratio) in their molecular formulas and have a characteristic odour. These are called aromatic compounds. It was observed that almost all the aromatic compounds have a six carbon unit in their molecules like benzene. Hence, benzene was recognized as the simplest and the parent member of this class of compounds.

However, it was soon realized that many aromatic compounds are odouriess whereas many others are fragrant though they are not aromatic. Further, when aromatic compounds of higher molecular mass were subjected to various methods of degradation, they often produced benzene or derivatives of benzene.

Q. Aromatic compounds burn with sooty flame. Justify.

Ans **Sooty Flame of Aromatic Compounds:**

Aromatic compounds have relatively high ratio of carbon to hydrogen. So, when they are burnt, they give sooty flame. The sooty flame is carbon particles.

$$2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O$$

On the other hand, if we burn methane (natural gas) in a normal supply of air, a blue flame with no sooty particles is formed.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Reason:

1 mole of benzene requires 7.5 moles of oxygen for complete combustion

1 mole of methane requires only 2 moles of oxygen

It means that the aliphatic compounds require a much lower volume of oxygen for complete combustion. So during the burning of aromatic compounds, some carbon remains in unburnt form which appear in the form of sooty flame.

Q.4 What are aromatic hydrocarbons? How are they classified?

Ans **Aromatic compounds:**

Aromatic hydrocarbons include benzene and all those compounds that are structurally related to benzene.



Arenes are strictly hydrocarbons.
Aromatic compounds can contain other functional groups.

Benzene has characteristics structural features. It has a regular planar hexagonal structure.

Classification of Aromatic Compounds

On the basis of the number of benzene rings aromatic hydrocarbons can be categorized into following classes.

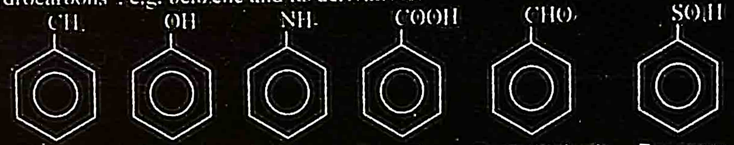
(a) Monocyclic Aromatic Hydrocarbons

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(b) Polycyclic Aromatic Hydrocarbons

(a) Monocyclic Aromatic Hydrocarbons

"Aromatic hydrocarbons containing one benzene ring in their molecules are called Monocyclic Aromatic Hydrocarbons". e.g. benzene and its derivatives.



Toluene, Phenol, Aniline, Benzoic acid, Benzaldehyde, Benzene-sulphonic acid

(b) Polycyclic Aromatic Hydrocarbons

"Aromatic hydrocarbons containing two or more benzene rings in their molecules are called Polycyclic Aromatic Hydrocarbons."

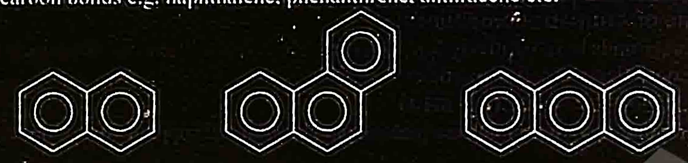
They may be divided into two main classes.

(i) Isolated rings: Those in which benzene rings are isolated e.g. biphenyl, diphenylmethane, etc.



Biphenyl, Diphenylmethane

(ii) Fused rings: Those in which the benzene rings are fused together at ortho positions so that the adjacent rings have a common carbon to carbon bonds e.g. naphthalene, phenanthrene, anthracene etc.



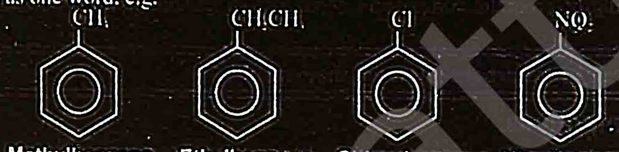
Naphthalene, Phenanthrene, Anthracene

NOMENCLATURE

(Monocyclic Aromatic Hydrocarbons and their Derivatives)

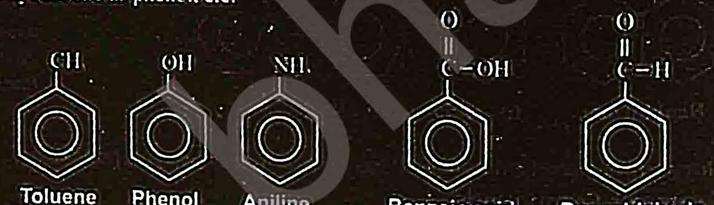
Some important rules of naming are given below.

1. Mono-substituted benzene derivatives are named by prefixing benzene with the name of the substituent. The whole name is written as one word. e.g.



Methylbenzene, Ethylbenzene, Chlorobenzene, Nitrobenzene

2. There are certain monosubstituted benzene derivatives which are given the special names, like methylbenzene as toluene, hydroxybenzene as phenol, etc.

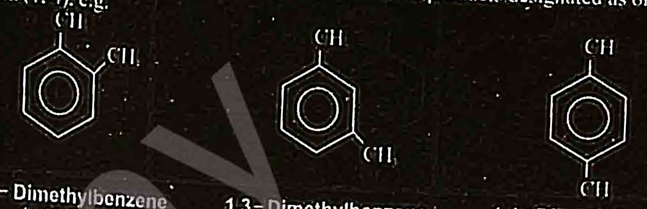


Toluene, Phenol, Aniline, Benzoic acid, Benzaldehyde

All the six position in benzene are exactly equivalent so there is only one monosubstituted benzene.

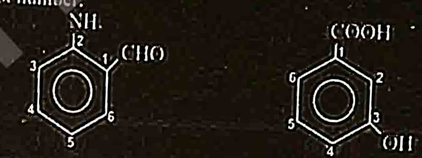
o When a hydrogen atom is removed from benzene, we get a phenyl group symbolized by C_6H_5- or Ph –. Substituted phenyl groups are called **aryl groups.**

3. The second substituent in benzene would give rise to three isomeric products designated as ortho (1, 2), meta (1, 3) and para (1, 4), e.g.



1,2 – Dimethylbenzene (o-Xylene), 1,3 – Dimethylbenzene (m-Xylene), 1,4 – Dimethylbenzene (p-Xylene)

4. If two or more substituents are different, then the substituent that is treated as a high priority group, is given the number 1 position in the benzene ring. Other groups are numbered by counting from position 1 in the manner which gives them the lowest number.



2-Aminobenzaldehyde, 3-Hydroxybenzoic acid

(The order of priority of the groups (left to right)

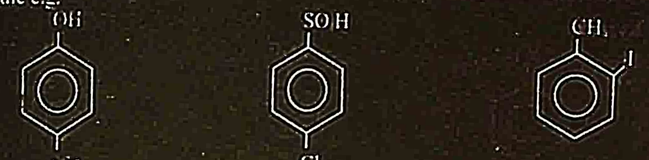
$-COOH, -CN, -CHO, -COCH_3, -OH, -NH_2, -OR, -R$.

5. If two substituents are different and they are not present in priority order list, they are named in alphabetical order. The last named substituent will be at position 1, e.g.



3-Chloroiodobenzene, 2-Bromonitrobenzene

6. If there is a substituent on the ring which gives a special name to the molecule, then special name is used as parent name to the molecule e.g.



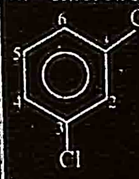
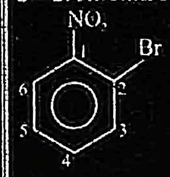
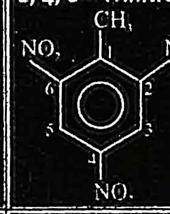
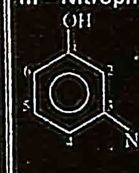
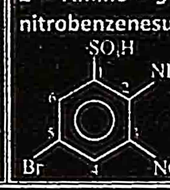
4-Aminophenol, 4-Chlorobenzenesulphonic acid, 2-Iodotoluene

Q7. (a) Draw structural formulas for the following compounds:

(i) m-Chlorobenzoic acid (ii) p-Hydroxybenzoic acid
(iii) o-Bromonitrobenzene (iv) o-Ethyltoluene
(v) p-Nitroaniline (vi) 2,4,6-Trinitrotoluene
(vii) m-Nitrophenol (viii) p-Dibenzylbenzene
(ix) 2-Amino-5-bromo-3-nitrobenzenesulphonic acid

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Ans.

(i) m - Chlorobenzoic Acid 	(ii) p - Hydroxybenzoic Acid 	(iii) o – Bromonitrobenzene 
(iv) O - Ethyltoluene 	(v) p – Nitroaniline 	(vi) 2, 4, 6 – Trinitrotoluene 
(vii) m – Nitrophenol 	(viii) p – Dibenzylbenezene 	(ix) 2 – Amino - 5- bromo – 3 – nitrobenzenesulphonic acid: 

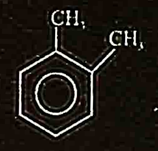
Q.7(b) Give names and the possible isomeric structures of the following:

(i) Xylene (ii) Trimethylbenzene (iii) Bromonitrotoluene

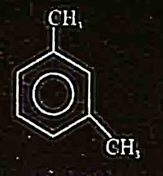
Ans. If two (CH_3) groups are allocated with a benzene ring, the compound is called as xylene.

b) Give names and possible isomers.

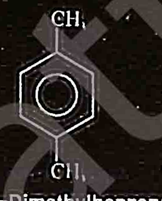
i. Isomers of Xylene



1,2—Dimethylbenzene (o-xylene)

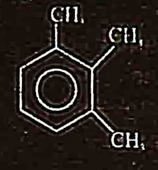


1,3—Dimethylbenzene (m-xylene)

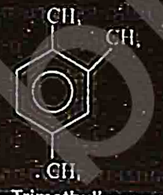


1,4—Dimethylbenzene (p-xylene)

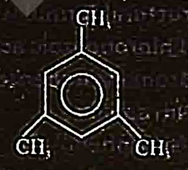
ii. Isomers of Trimethylbenzene



1,2,3—Trimethylbenzene



1,2,4—Trimethylbenzene



1,3,5—Trimethylbenzene

iii. Isomers of Bromonitrotoluene

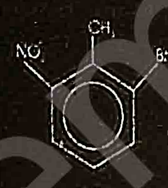


2-Bromo 3-nitrotoluene

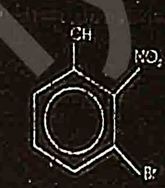
2-Bromo 4-nitrotoluene



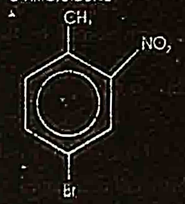
2-Bromo 5-nitrotoluene



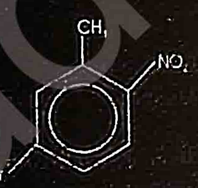
3-Bromo 6-nitrotoluene



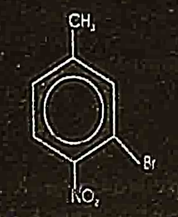
3-Bromo 2-nitrotoluene



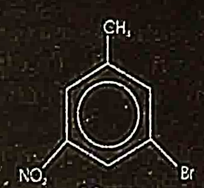
4-Bromo 2-nitrotoluene



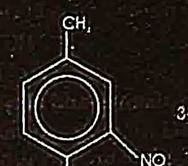
5-Bromo 2-nitrotoluene



3-Bromo 4-nitrotoluene

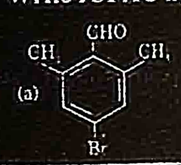


3-Bromo 5-nitrotoluene

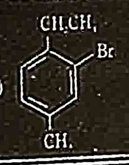


4-Bromo 3-nitrotoluene

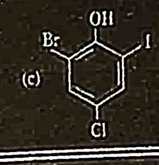
Q8. Write IUPAC names of the following molecules.



(a)



(b)



(c)

Ans:

(a)



4-Bromo-2, 6-dimethylbenzaldehyde

(b)



3 – Bromo – 4 – ethyltoluene

(c)



6-Bromo-4-chloro-2-iodophenol

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BENZENE

Discovery

- Benzene was discovered by **Michael Faraday** in 1825 in the gas produced by the destructive distillation of vegetable oil.
- Twenty years later it was also found in coal-tar by **Hoffmann.**

STRUCTURE OF BENZENE

Molecular Formula

(i) The empirical formula of benzene is determined by the **elemental analysis**, which is CH. So its empirical formula mass is (CH = 12 + 1 = 13)

(ii) Its molecular mass determined by the **vapour density method** is 78.108 amu. Therefore, the molecular formula of benzene is C_6H_6.

Molecular formula = n × Empirical formula

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{78.108}{13} = 6$$

Molecular formula = 6 × CH

Molecular formula = C_6H_6

(iii) The molecular formula of benzene indicates that it is highly unsaturated compound.

Straight Chain Structure Ruled Out

(i) Straight chain formulas

Two of the possible straight chain formulas suggested for benzene are:

$HC \equiv C - CH_2 - CH_2 - C \equiv CH$ (1, 5 – Hexadiyne)

$H_2C = CH - C \equiv C - CH = CH_2$ (1, 5 – Hexadiene – 3 – yne)

Comparison with alkenes and alkynes

A compound having a structure as above should behave like an alkene or alkyne. Both are oxidized by alkaline $KMnO_4$ solution, while benzene is stable to $KMnO_4$ solution. It does not decolorize $KMnO_4$ solution.

- **Benzene** gives addition reactions with hydrogen and halogens, which indicate the presence of three double bonds.
- **Benzene** also gives substitution reactions with conc. HNO_3 and conc. H_2SO_4 which indicate that benzene has a saturated structure.

(ii) Monosubstituent product

Considering a straight chain structure for benzene and further assuming that each carbon carries one H – atom, it should be capable of forming three mono substitution products.

X – C.C.C.C.C.C X – C(C).C.C.C.C X – C(C).C.C.C.C

But benzene yields only one monosubstituent product.

(iii) General formula

The molecular formula of benzene C_6H_6 does not obey any of the open chain hydrocarbons, such as alkane C_nH_{2n+2} (C_6H_{14}), alkene C_nH_{2n} (C_6H_{12}) or alkyne C_nH_{2n-2} (C_6H_{10}).

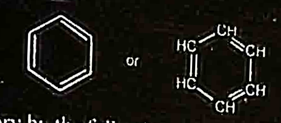
Conclusion

It means benzene does not belong to open chain hydrocarbons and therefore possibility of a straight chain structure is ruled out.

Kekule's Structure

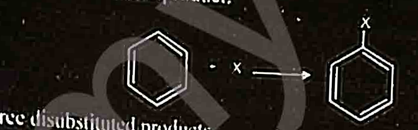
The structure of benzene continued to be a serious problem for chemists for about 40 years. A German chemist Kekule at last solved the problem in 1865. Kekule proposed

"A cyclic regular hexagonal structure for benzene, which contains three double bonds alternating with three single bonds."

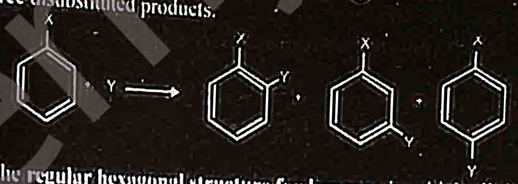


He supported his theory by the following arguments.

(i) Benzene gives only one monosubstituted product.



(ii) Benzene gives only three disubstituted products.

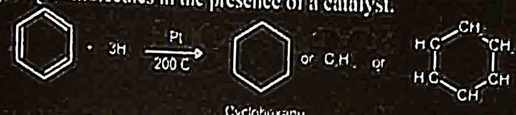




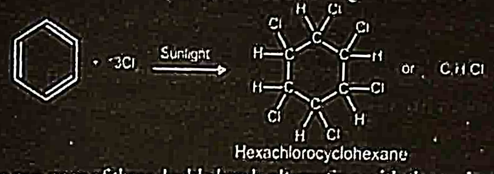
A snake biting its tail featured in Kekule's inspirational dream.

These points confirm the **regular hexagonal structure for benzene** in which all the carbon atoms are occupying identical positions in the molecule. Therefore, benzene forms only one toluene, one nitrobenzene and one phenol.

(iii) Benzene adds three hydrogen molecules in the presence of a catalyst.



(iv) Benzene adds three molecules of chlorine in the presence of sunlight.

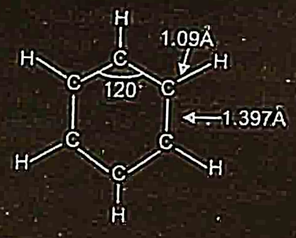


These two reactions confirm the presence of three double bonds alternating with three single bonds.

X-Ray Studies Of Benzene Structure

The X-ray studies of benzene have confirmed that:

- Benzene has regular hexagonal structure.
- All the carbon and hydrogen atoms are in the same plane.
- All the angles are of 120°.
- All C – C and C – H bond lengths are 1.397Å and 1.09 Å, respectively.



Objections to Kekule's Formula

Kekule's formula with three double bonds demands a high degree of unsaturation from benzene while usually it exhibits a saturated character. Thus benzene yields substitution products readily and forms addition products reluctantly. Benzene is also a very stable compound.

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Q. 10. Describe the structure of benzene on the basis of following:
(i) Atomic orbital treatment (ii) Resonance method.

Modern Concepts about the Structure of Benzene

(Atomic Orbital Treatment of Benzene)

The hexagonal frame-work of benzene can be conveniently explained using hybridization approach. According to atomic orbital hybridization:

(i) Each carbon in benzene is sp^2 hybridized.

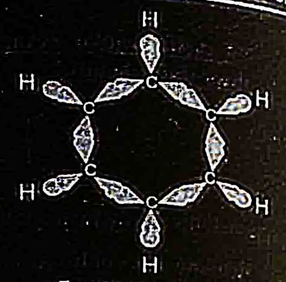
(ii) The three sp^2 hybrid orbitals on each carbon are utilized to form three σ bonds, two with adjacent carbon atoms and one with hydrogen.

(iii) The unhybridized 2p, orbitals remain at right angle to these sp^2 orbitals. Since all the sp^2 orbitals are in the same plane therefore all the carbon and hydrogen atoms are coplanar.

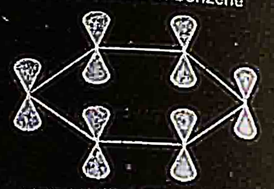
(iv) All the angles are of 120° which confirms the regular hexagonal structure of benzene.

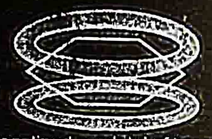
(v) The unhybridized 2p, orbitals partially overlap to form a continuous sheath of electron cloud, enveloping, above and below, the six carbon-carbon sigma bonds of the ring.

(vi) Since each 2p, orbital is overlapped by the 2p, orbitals of adjacent carbon atoms, therefore, this overlapping gives 'diffused' or 'delocalized' electron cloud.



σ-Framework of benzene


Unhybridized $2P_z$ orbitals

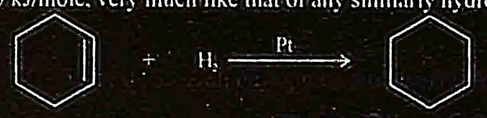

Delocalized π-orbital of benzene

The Stability of Benzene

Benzene is an extraordinary stable molecule. This stability is due to the extensive **delocalization of electron cloud.** The extent of stability of benzene can be measured by comparing it with hypothetical compound, 1,3,5–cyclohexatriene. Stability of benzene is determined by estimating the heat of hydrogenation (ΔH).

(i) ΔH for Cyclohexene

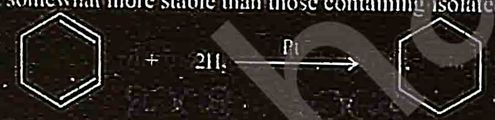
Cyclohexene, can be easily hydrogenated to give cyclohexane. When the ΔH for this reaction is measured it is found to be – 119.5 kJ/mole, very much like that of any similarly hydrogenated alkene.



Cyclohexene Cyclohexane ΔH = –119.5 kJ / mol

(ii) ΔH for 1,3-Cyclohexadiene

We would expect that hydrogenation of 1,3 – Cyclohexadiene would liberate roughly twice as much heat and thus have ΔH equal to –239 kJ/mol. When this experiment is done, the result is ΔH = -231.5kJ/mole. This result is quite close to what we calculated, and the difference can be explained by taking into account the fact that compounds containing conjugated double bonds are usually somewhat more stable than those containing isolated double bonds.

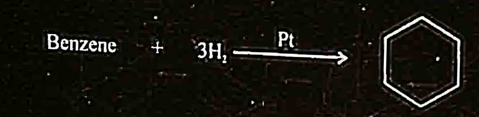


1,3-Cyclohexadiene Cyclohexane

Calculated ΔH = 2 × (–119.5) = –239kJ/mole
Observed ΔH = –231.5kJ/mole

(iii) ΔH for 1,3,5-Cyclohexatriene

If benzene is simply 1.3.5 – Cyclohexatriene, we would predict that benzene would liberate approximately - 358.5kJ/mole (3 x – 119.5) when it is hydrogenated. When the experiment is actually done, the result is surprisingly different. The reaction is exothermic but only be – 208kJ/mole.

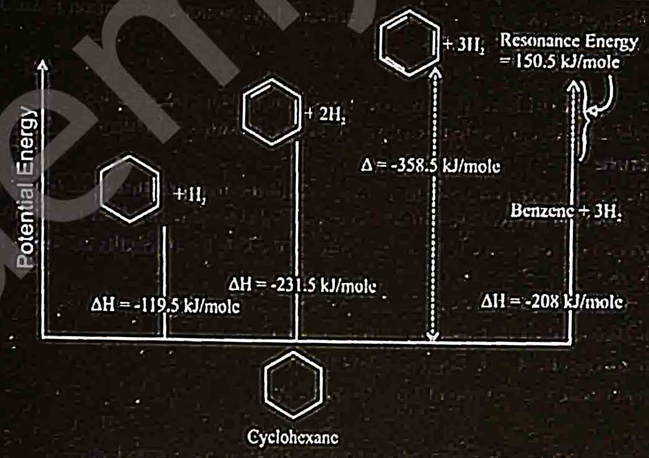


Cyclohexane ΔH = –208 kJ / mol

Calculated ΔH = (3x -119.5) = -358.5kJ/mole
Observed ΔH = -208 kJ/mole
Difference = 150.5kJ/mole

Stability diagram

When the results are represented by the following figure, it becomes clear that benzene is much more stable than we calculated it to be.



Relative stabilities of Cyclohexene, 1,3-Cyclohexadiene, 1,3,5-Cyclohexatriene (hypothetical) and benzene.

Resonance energy

The difference of energy between hypothetical compound i.e., (1, 3, 5 – cyclohexatriene) and actual compound i.e. (benzene) is called resonance energy. Indeed, benzene is more stable than the hypothetical 1, 3, 5-cyclohexatriene by 150.5 kJ/mole. Greater the resonance energy greater the stability of the compound. It means benzene shows the phenomenon of resonance which makes it more stable than others. In benzene electrons are delocalized making it a very stable molecule.

The Resonance Method

Resonance

"The possibility of different pairing schemes of valence electrons of atoms is called resonance"

or

"The situation in which two or more plausible Lewis structures can be written but the actual structure cannot be written is called Resonance."

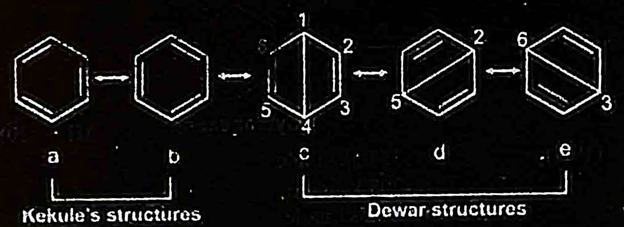
The resonance is represented by a double headed arrow (↔).

Resonance structures

The different structures arranged as a result of resonance are called "Resonance structures".

Example: The following different pairing schemes of the fourth valence (the π – electrons) of carbon atoms are possible in benzene. The stability of a molecule increases with increase in the number of its resonance structures. Thus molecule of benzene is chemically quite stable.

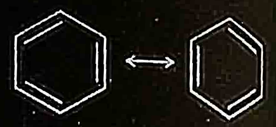
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Dewar's structures

In Dewar structures, the carbon atoms at opposite positions 1-4, 2-5 and 3-6 are at larger distances than those in the adjacent positions 1-2, 2-3, 3-4, 4-5, 5-6 and 6-1. Therefore the bondings between C_1-C_4, C_2-C_5 and C_3-C_6 are not favourable energetically. Hence the Dewar structures for benzene have minor contribution towards the actual structure of benzene.

Kekule's structures



Kekule's structure (a) and (b) have the larger contribution in benzene sructure. Therefore, benzene molecule can be represented by either of the two Kekule's structures.

Resonance Hybrid structure

Infact, the structure of benzene is a resonance hybrid of all the five structures (a), (b), (c), (d) and (e). The three alternate single and double bonds in the Kekule's structures are called conjugate bonds or resonating bonds.

Since the structure of benzene is a resonance hybrid, therefore all the C-C bond lengths are equal but different from those in alkanes, alkenes and alkynes.

In alkanes the C – C bond length is 1.54Å.
In alkenes the C = C bond length is 1.34Å.
In alkynes the C ≡ C bond length is 1.20Å.
In benzene the C–C bond length is 1.397 Å.



Benzene

Conclusion

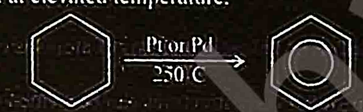
- The C – C bond length in benzene is intermediate between those in alkanes and alkenes.
- The resonating single and double bonds in benzene can better be represented as a complete circle inside the ring.

Preparation of Benzene

Benzene and other aromatic hydrocarbons are readily obtained in large quantities from coal and petroleum. Benzene and some other hydrocarbons can also be obtained from petroleum by special cracking methods. Some of the methods generally used for the preparation of benzene are as follows.

1. Dehydrogenation of Cyclohexane

When cyclohexane or its derivative is dehydrogenated we get benzene or a substituted benzene. The reaction is carried out in the presence of catalyst at elevated temperature.



Cyclohexane → Benzene

2. From Acetylene (polymerization)

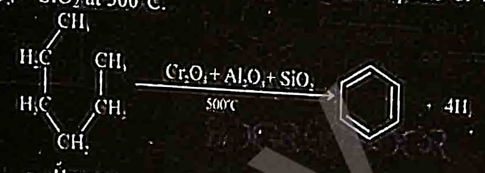
Benzene is formed by passing acetylene under pressure over an organo-nickel catalyst at 70°C.



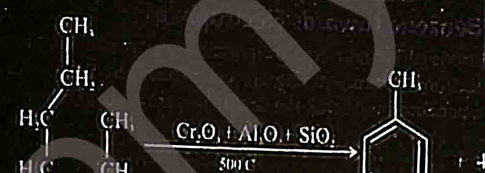
Acetylene → Benzene

3. From Alkanes (Aromatization)

Benzene and toluene are also prepared by passing the vapours of n-hexane or n-heptane over a mixture of catalysts $Cr_2O_3 + Al_2O_3 + SiO_2$ at 500°C.



n - Hexane → Benzene



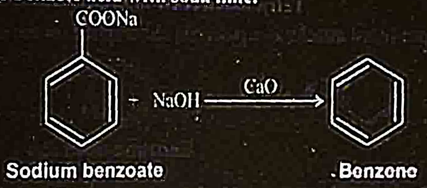
n - Heptane → Toluene

Aromatization
n-Heptane → Toluene
Octane no. = 0 Octane no. = 109

4. Preparation in the Laboratory

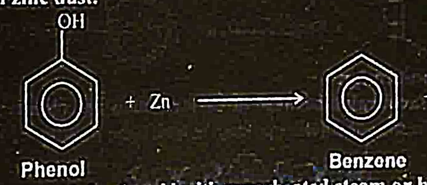
Benzene can be prepared in the laboratory by any one of the following methods.

(i) By heating sodium salt of benzoic acid with soda lime.



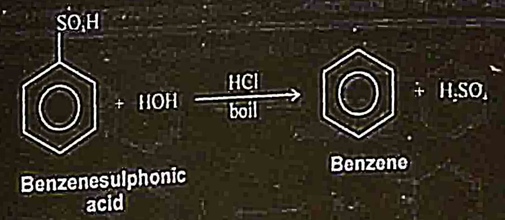
Sodium benzoate → Benzene

(ii) By distilling phenol with zinc dust.



Phenol → Benzene

(iii) By the hydrolysis of benzenesulphonic acid with superheated steam or by boiling with dil. HCl.

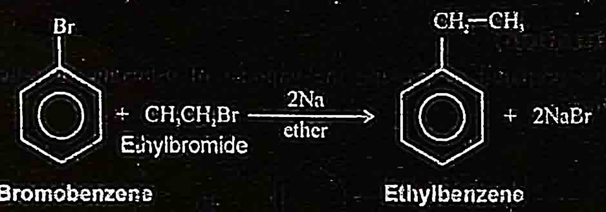


Benzenesulphonic acid → Benzene

5. Wurtz-Fittig Reaction

The Wurtz reaction for the synthesis of alkanes was extended by Fittig in 1864 to the synthesis of alkyl aromatic hydrocarbons.

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Bromobenzene Ethylbenzene

Wurtz Synthesis:

$2CH_3-CH_2-Cl + 2Na \xrightarrow{Ether} CH_3-CH_2-CH_2-CH_3 + 2NaCl$

- Useful for the preparation of symmetrical alkanes.

REACTIONS OF BENZENE

General Pattern of Reactivity of Benzene towards Electrophiles

The highly stable, delocalized electrons of benzene ring are not readily available for the nucleophillic attack like the electrons of alkenes. Therefore, the electrons of benzene ring are not attacked by weak electrophiles. It means that more powerful electrophiles are required to penetrate and break the continuous sheath of electron cloud in benzene.

Electrophile in halogenation

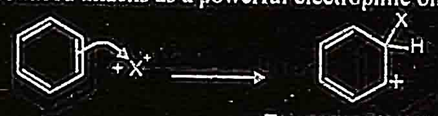
- Substitution of halogen in benzene requires iron or corresponding ferric halide as a catalyst.
- Infact iron too is first converted into FeX_3 which further reacts with halogen molecule to produce a powerful electrophile.

$$2Fe + 3X_2 \longrightarrow 2FeX_3$$

$$FeX_3 + X_2 \longrightarrow FeX^-_4 + X^+$$

Tetra haloferrate ion (III) (Halogenonium ion)

- The halogenonium ion X^+ thus produced attacks as a powerful electrophile on the electrons of benzene ring.



Benzenonium ion



Benzenonium ion

- **The addition product is not favourable because in its formation the characteristic stability of benzene is lost.** The only possible product is the substitution product in which the stability of benzene is retained.

Q. Write down general mechanism of electrophilic substitution reactions of benzene?

Ans: The general pattern of the chemical reactivity of benzene towards electrophiles can be shown as follows.

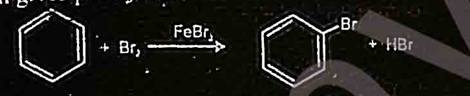


Electrophilic Substitution Reactions of Benzene

1. Halogenation

The introduction of halogen group in benzene ring is called "Halogenation"

- Benzene reacts with halogen in the presence of a catalyst like $FeBr_3$, $AlCl_3$, etc.
- Chlorination and bromination are normal reactions but fluorination is too vigorous to control.
- Iodination gives poor yield.



Bromobenzene

Similarly,

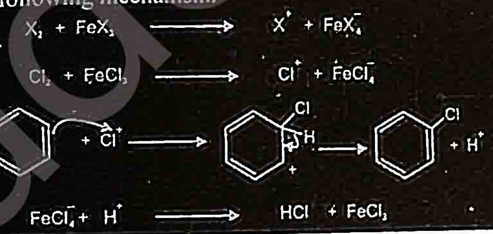


Chlorobenzene

Nucleophile	Electrophile
• Negatively charged ions (anions) are nucleophiles. e.g. Cl^-, H^-, Br^-, SO_4^{-2} etc	• Positively charged ions (cations) are electrophiles e.g. H^+, Cl^+, Br^+, NH_4^+
• Neutral molecules in which central atom have lone pairs of electrons. e.g. $\ddot{P}Cl_3$, $\ddot{P}H_3$, $\ddot{S}O_2$, $\ddot{N}H_3$, $H_2\ddot{O}$ etc.	• Neutral molecules in which central atom is electron deficient. e.g. BH_3, BF_3, $BeCl_2$, $AlCl_3$, $ZnCl_2$, $FeCl_3$ etc.
• Lewis bases are usually nucleophiles.	• Lewis acids are usually electrophiles.
• The molecules which contain pi electrons in their structures act as nucleophiles. e.g. ethene, benzene etc.	• Neutral molecules in which central atom contains partial positive charge act as electrophiles. e.g. PCl_5, SO_3, CO_2 etc.

Mechanism:

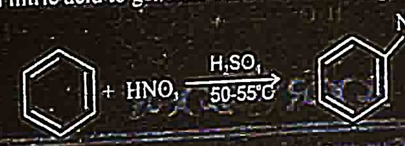
The actual halogenating agent is X^+ (i.e. Cl^+ or Br^+) is formed by the following mechanism.



2. Nitration:

The introduction of nitro group (NO_2) in benzene ring is called "Nitration".

- The nitration of benzene takes place when it is heated with a 1:1 mixture of conc. HNO_3 and conc. H_2SO_4 at 50-55°C.
- Sulphuric acid reacts with nitric acid to generate nitronium ion (NO_2^+).



Mechanism:



Nitrobenzene

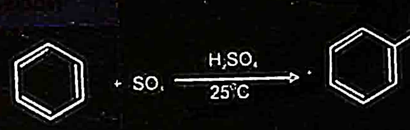
3. Sulphonation:

The introduction of sulphonic acid group in benzene ring is called "Sulphonation".

When benzene is heated with fuming H_2SO_4 or conc. H_2SO_4, it yields benzene sulphonic acid.



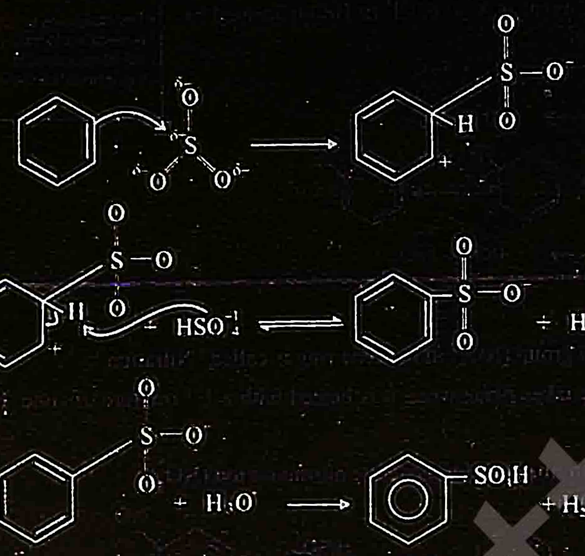
Benzenesulphonic acid



Mechanism:

When sulphuric acid alone is used, the actual electrophile in this reaction is SO_3

$$H_2SO_4 + H_2SO_4 \rightleftharpoons H_3O^+ + SO_3 + HSO_4^-$$



Q.15 What are Friedel–Crafts reactions? Give mechanism with example of the following reactions.

(i) Friedel–Crafts alkylation reaction (ii) Friedel –Crafts acylation reaction

4. Friedel-Crafts Reactions:

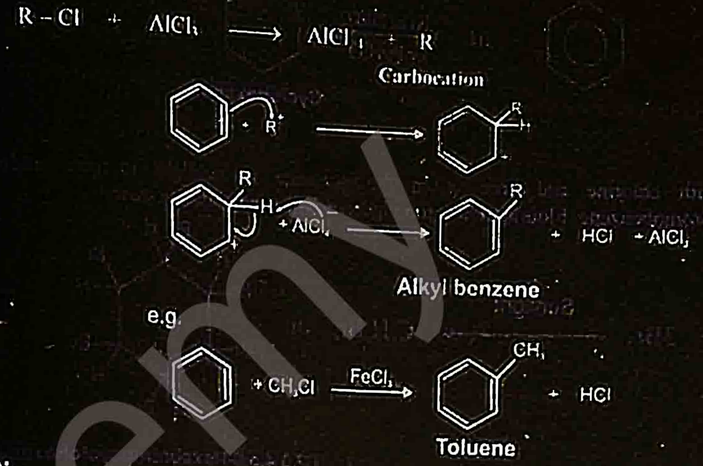
The alkylation and acylation of benzene are called Friedel-Crafts reactions.

(a) Alkylation:

The introduction of an alkyl group in the benzene ring in the presence of an alkyl halide and a catalyst $AlCl_3$ is called Friedel-Crafts alkylation or Alkylation.



Mechanism:



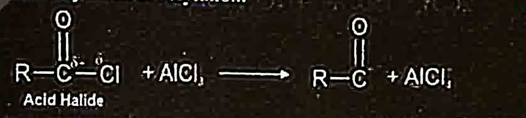
Alkyl benzene

e.g.

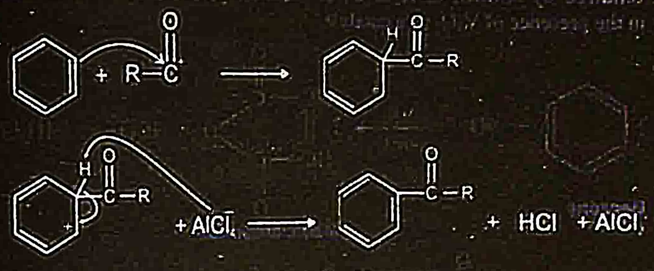
Toluene

(b) Acylation:

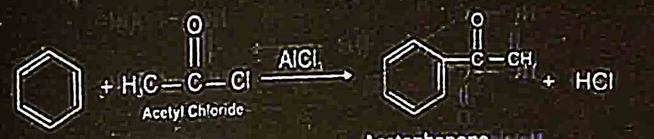
The introduction of an acyl group $R-\overset{O}{\overset{\|}{C}}-$ in the benzene ring in the presence of an acyl halide and a catalyst $AlCl_3$ is called Friedel Crafts acylation or Acylation.



Acid Halide



Acyl benzene



Acetyl Chloride

Acetophenone

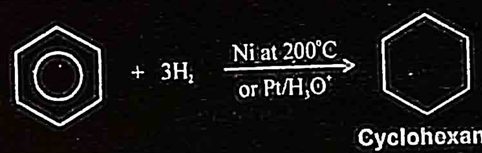
Reactions in which Benzene Ring is Involved

1. Addition Reactions

(a) Reduction:

Benzene is reduced to cyclohexane on heating at high temperature with hydrogen in the presence of Pt in an acidic solvent (acetic acid) or Ni at 200°C as a catalyst.

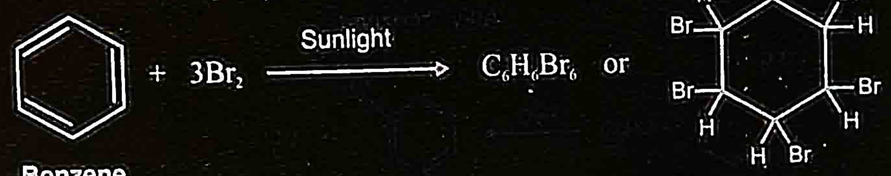
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Cyclohexano

(b) Halogenation:

Benzene reacts with chlorine and bromine in the presence of sunlight to give addition products, hexachlorobenzene or hexabromobenzene. Flourination is too vigorous while iodination is slow.



Benzene

1,2,3,4,5,6-Hexabromocyclohexane

(c) Combustion:

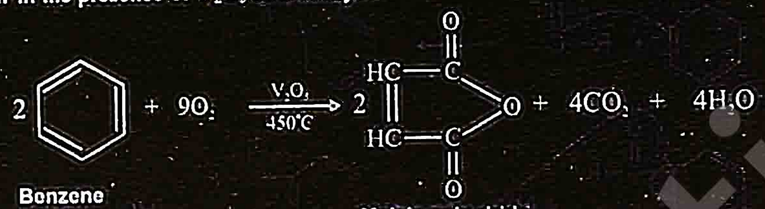
When benzene is burnt in free supply of air, it is completely oxidized to CO_2 and H_2O.

$$2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O$$

(d) Oxidation:

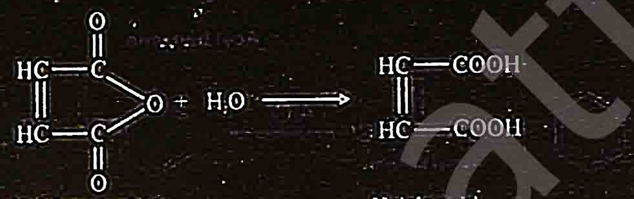
(i) Catalytic Oxidation:

Benzene is not oxidized by $KMnO_4$ or $K_2Cr_2O_7$ at room temperature. The ring is destroyed when benzene is strongly heated with air in the presence of V_2O_5 as a catalyst.



Benzene

Maleic anhydride



Maleic anhydride

Maleic acid

(ii) Ozonolysis:

Benezene reacts with ozone and gives glyoxal through benzene triozonide.



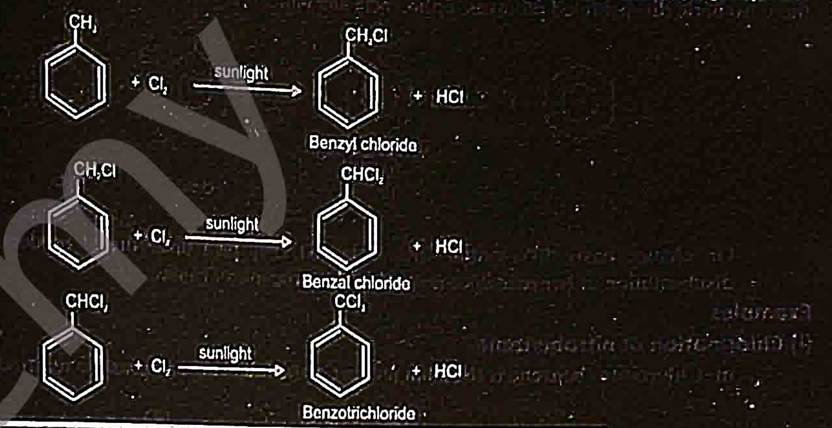
Benzene triozonide

Glyoxal

Side Chain Reactions of Alkyl Benzene

(i) Side chain substitution

When alkyl benzenes are treated with chlorine or bromine in the presence of sunlight, only the alkyl groups are substituted.



(ii) Side chain oxidation

Alkyl benzene are readily oxidized by acidified $KMnO_4$ or $K_2Cr_2O_7$. In these reactions, the alkyl groups are oxidized keeping the benzene ring intact.



Toluene

Benzoic acid

Whatever the length of an alkyl group may be it gives only one carboxyl group. Moreover, the colour of $KMnO_4$ is discharged. **Therefore this reaction is used as a test for alkylbenzenes.**



Ethylbenzene

Benzoic acid

Q. How would your convert benzene into benzoic acid?
Q. Distinguish between benzene and toluene.

Q5. What happens When:

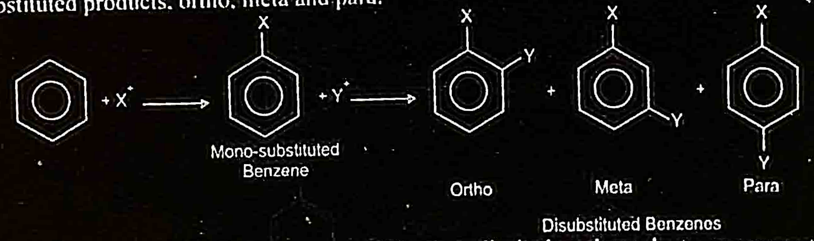
(a) Benzene is heated with conc. H_2SO_4 at 250°C.
(b) Chlorine is passed through benzene in sunlight.
(c) A mixture of benzene vapours and air are passed over heated vanadium pentaoxide.
(d) Benzene is burnt in free supply of air.

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Orientation in Electrophilic Substitution reactions

Substituted benzene product

When an electorphilic substitution reaction takes place on benzene ring, we get only one monosubstituted benzene because all the six position in the ring are equivalent. However, the introduction of a second group into the ring may give three isomeric disubstituted products, ortho, meta and para.



On chance basis 40% ortho, 40% meta and 20% para disubstituted products are expected. But the actual disubstitution of benzene does not follow this principle of chance.

Examples

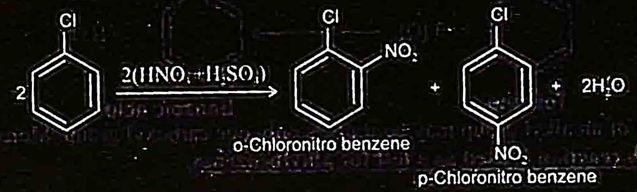
(i) Chlorination of nitrobenzene

m–Chloronitro benzene is the main product of the following halogenation reaction.



(ii) nitration of chlorobenzene

A mixture of o-Chloronitrobenzne and p-Chloronitrobenzene is obtained from the nitration of chlorobenzene.



Conclusion

It means that the group present in the mono-substituted benzene ring has the directive effect and thus determines the position or orientation for the new incoming groups. Therefore, there are two types of groups:

1. ortho- and para- directing groups 2. meta- directing groups

1. ortho and para Directing Groups

- These groups release electrons to the benzene ring, thereby facilitating the availability of electrons to the electrophiles at ortho and para positions.
- This results in the increased chemical reactivity of benzene ring towards electrophiles.
- The benzene ring can offer more than one positions (ortho and para) to the new incoming groups.
- These groups are called ortho and para directing groups.

Example: Nitration of toluene



The electron releasing effect of methyl group is significant and it makes the ring a good nucleophile. Due to this increased reactivity, more nitro groups can enter the ring.





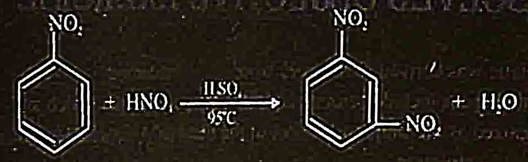
Other examples of ortho and para directing groups:

$-N(CH_3)_2$, $-NH_2$, $-OH$, $-OCH_3$, $-Cl$, $-Br$, $-I$

2. meta-Directing Groups

- These groups withdraw the electrons of the benzene ring towards themselves, thereby decreasing their availability to the electrophiles. This results in the decreased chemical reactivity of benzene.
- Due to the electron withdrawing effect of such substituents, the ortho and para positions are become more electron deficient than the meta position. Thus the incoming electrophile will prefer to attack on meta position rather than ortho and para positions. These groups are called meta-directing groups.

Example: Nitration of nitrobenzene



- The substitution of third nitro group is not possible.
- **Other examples of meta directing groups are:**

$-N^+R_3$, $-C\equiv N$, $-COOH$, $-CHO$, $-COR$

Comparison Of Reactivities Of Alkanes, Alkenes And Benzene

- We have studied that alkanes are unreactive class of compounds and their unreactivity is due to their **non-polar nature** and the **inertness of σ-bond**. However, they undergo substitution reactions relatively easily and these reactions involve free radicals.
- Alkenes, on the other hand, are very reactive class of compounds and their reactivity is due to the inherent **weakness of the π-bond** and the **availability of π electrons** for the electrophilic reagents. They undergo electrophilic addition reactions easily. Being relatively unstable, alkenes undergo polymerization reactions and they are also readily oxidized.

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- Benzene is unique in its behaviour. It is highly unsaturated compound and at the same time it is very stable molecule. The stability of benzene, as described earlier, is due to the extensive delocalization of π-electrons. It resembles alkenes when it gives addition reactions. The substitution of benzene, however, does not involve free radicals. **These are electrophilic substitution reactions and involve electrophiles.**

Its addition reactions require more drastic conditions than those for alkenes.

Benzene does not undergo polymerization and it is also resistant to oxidation.

Alkenes > Benzene > Alkanes

KEY POINTS

1. Aromatic hydrocarbons include benzene and all those compounds that are structurally related to benzene.
2. Aromatic hydrocarbons containing one benzene ring in their molecules are called monocyclic aromatic hydrocarbons.
3. Aromatic hydrocarbons containing two or more benzene rings in their molecules are called polycyclic aromatic hydrocarbons.
4. Benzene was discovered by Michael Faraday in 1825.
5. The electrons in benzene are loosely held and the ring acts as a source of electrons. Hence benzene is readily attacked by electrophiles in the presence of a catalyst.
6. Since electrophilic substitutions reaction lead to resonance stabilized benzene derivatives so substitutions are the main reactions of benzene.
7. Resonance energy of benzene is 150.5 kJ/mole.
8. Structure of benzene is the resonance hybrid of two Kekule's structures and three Dewar's structures.
9. Groups like NH_2, NHR, – OR, –SH, – OCOR, – X, – OH, etc. which increase the electron density in the nucleus and facilitate further electrophilic substitutions are known as ortho- and para-directing groups.
10. Groups like CN, – CHO, NH_3, NR_3, CCl_3 which hinder further substitution in the benzene nucleus are known as meta- directing groups.

SOLVED OBJECTIVE EXERCISE

Q1. Fill in the blanks.

(i) The term aromatic was derived from Greek word _____ meaning _____.
(ii) Aromatic hydrocarbons include benzene and all those compounds which are _____ related to benzene.
(iii) _____ is recognized as the simplest member of the class of Aromatic Hydrocarbons.
(iv) Benzene has _____ structure.
(v) The removal of hydrogen atom from aromatic hydrocarbons gives a radical. The radicals are called ____.
(vi) Benzene was discovered by Michael Faraday in ____
(vii) The unhybridized $2p_z$ orbitals in benzene partially overlap to form a _____ of electron could.
(viii) The introduction of halogen group in benzene ring is called _____.
(ix) The molecular formula of C_6H_6 indicated that it is highly _____ compound.
(x) On oxidation in the presence of V_2O_5 benzene gives _____.

Answer Key.

(i)	Aroma, fragrant	(ii)	Structurally
(iii)	Benzene	(iv)	Regular hexagonal planar
(v)	Aryl groups	(vi)	1825
(vii)	Continuous sheath	(viii)	Halogenation
(ix)	Unsaturated	(x)	Maleic anhydride

Q2. Indicate True or false.

(i) Benzene is more reactive than alkene and less reactive than alkane.

(ii) Benzene has a pentagonal structure.
(iii) The C-C bond length in benzene molecule is 1.397 $\mathring{A}$.
(iv) The state of hybridization of carbon in benzene molecule is sp^3.
(v) There are six sigma bonds in benzene molecule.
(vi) Halogenonium ion produced in electrophilic substitution reactions is a powerful electrophile.
(vii) In electrophilic substitution reactions, addition products are favourable.
(viii) Sulphonation is carried out when benzene is heated with conc. HNO_3.
(ix) In ozonolysis benzene directly gives glyoxal.
(x) Benzene has five resonance contributing structures.

Answer Key.

(i)	False	(ii)	False	(iii)	True	(iv)	False	(v)	False
(vi)	True	(vii)	False	(viii)	False	(ix)	False	(x)	True

Q3. Multiple choice questions. Encircle the correct answer.

(i) **The benzene molecule contains**
(a) Three double bonds (b) Two double bonds
(c) One double bond (d) Delocalized π - electron charge

(ii) **Aromatic hydrocarbons are the derivatives of**
(a) Normal series of paraffins (b) alkene
(c) benzene (d) cyclohexane

(iii) **Which of the following acid can be used as a catalyst in Friedel - Crafts reactions?**
(a) $AlCl_3$ (b) HNO_3 (c) $BeCl_2$ (d) NaCl

(iv) **Benzene cannot undergo:**
(a) Substitution reaction (b) addition reactions
(c) oxidation reactions (d) elimination reactions

(v) **Amongst the following the compound that can be most readily sulphonated is:**
(a) toluene (b) benzene (c) nitrobenzene (d) chlorobenzene

(vi) **During nitration of benzene the active nitrating agent is:**
(a) NO_3 (b) NO_2^+ (c) NO_2^- (d) HNO_3

(vii) **Which compound is the most reactive one:**
(a) Benzene (b) ethene (c) ethane (d) ethyne

(viii) **The electrophile in aromatic sulphonation is:**
(a) H_2SO_4 (b) HSO_3 (c) SO_3 (d) SO_3^+

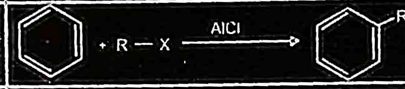
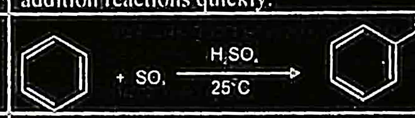
(ix) **Aromatic compounds burn with sooty flame because:**
(a) They have high percentage of hydrogen (b) They have a ring structure.
(c) They have high percentage of carbon (c) They resist reaction with air

(x) **The conversion of n-hexane into benzene by heating in the presence of Pt is called:**
(a) Isomerization (b) Aromatization (c) Dealkylation (d) Rearrangement

Solved Exercise MCQ's

Q.No:	Answers	Reason
(i).	(d) Delocalized π – electron charge	 Delocalized π-orbital of benzene

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(ii).	(c) benzene	
(iii).	(a) $AlCl_3$	
(iv).	(d) Elimination reaction	Benzene gives substitution reactions, oxidation reactions as well as addition reactions. As it is very stable so elimination is not possible.
(v).	(a) Toluene	Toluene is electron donating group and increase the availability of electrons at o and π – positions. Therefore, the rate of reaction is very high.
(vi).	(b) NO_2^+	NO_2^+ is strong electrophile and attacks on benzene ring first.
(vii).	(b) Ethene	Ethene $(CH_2 = CH_2)$ has more diffused and loosely held π – electrons and gives addition reactions quickly.
(viii).	(c) SO_3	
(ix).	(c) They have high percentage of carbon	$2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O + Heat$ Due to high percentage of carbon they give sooty flame due to unburnt carbon.
(x).	(b) Aromatization	The conversion of Aliphatic compounds into aromatic compounds is aromatization.e.g. n-Heptane ⟶ Toluene This process is used to increase octane number

Solved Answers TO Exercise

Q11. Predict the major products of bromination of the following compounds.
(a) Toluene (b) Nitrobenzene (c) Bromobenzene
(d) Benzoic acid (e) Benzaldehyde (f) Phenol

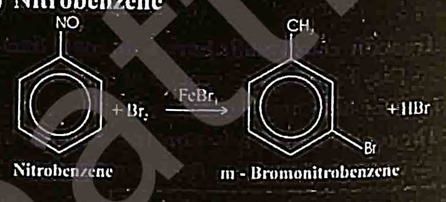
Ans.

(a) Toluene



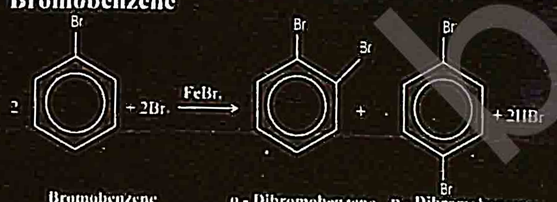
Toluene — o - Bromotoluene — p - Bromotoluene

(b) Nitrobenzene



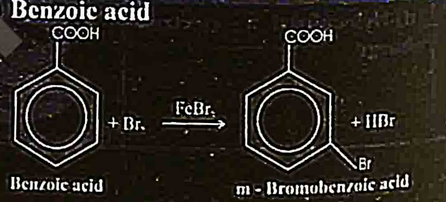
Nitrobenzene — m - Bromonitrobenzene

(c) Bromobenzene



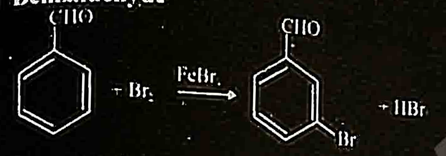
Bromobenzene — o - Dibromobenzene — p - Dibromobenzene

(d) Benzoic acid



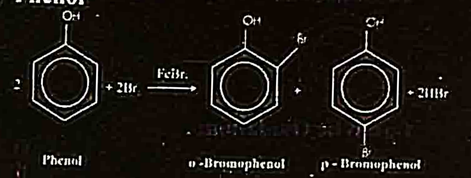
Benzoic acid — m - Bromobenzoic acid

(e) Benzaldehyde



Benzaldehyde — m-Bromobenzaldehyde

(f) Phenol



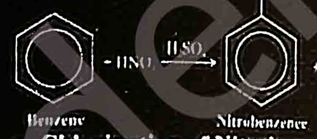
Phenol — o -Bromophenol — p - Bromophenol

Q12. How will you prepare the following compounds from benzene in two steps.
(a) m – Chloronitrobenzene (b) p – Chloronitrobenzene

Ans. a)

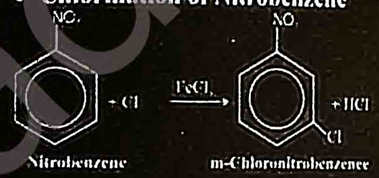
(a) m-Chloronitrobenzene

o Nitration of Benzene



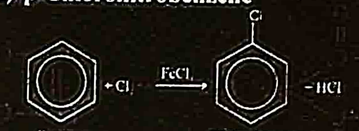
Benzene — Nitrobenzene

o Chlorination of Nitrobenzene

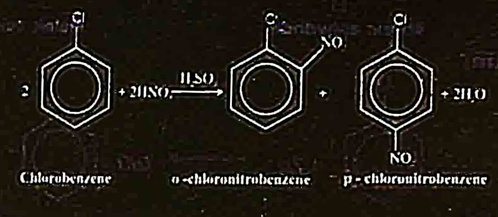


Nitrobenzene — m-Chloronitrobenzene

(b) p-Chloronitrobenzene

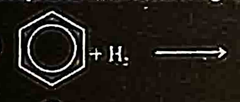


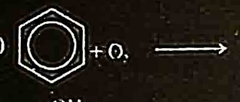
Benzene — Chlorobenzene

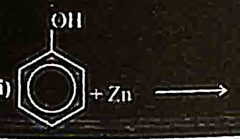


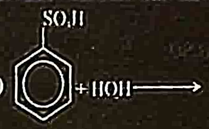
Chlorobenzene — o -chloronitrobenzene — p - chloronitrobenzene

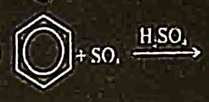
Q13. Complete the following reactions. Also mention the conditions needs to carry out these reactions.

(i) 

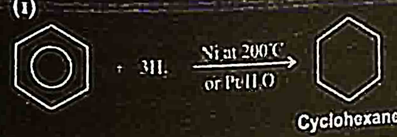
(ii) 

(iii) 

(iv) 

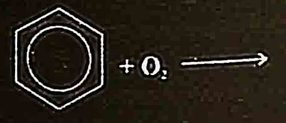
(v) 

Ans. (i)



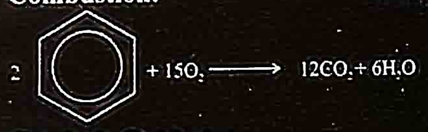
Cyclohexane

(ii)

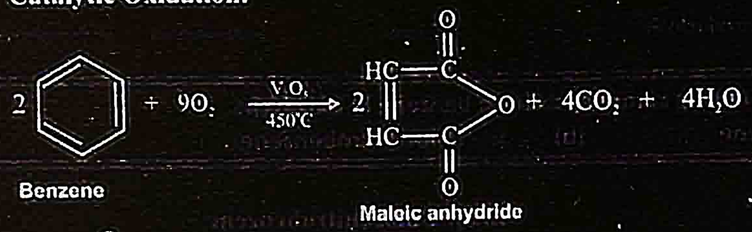


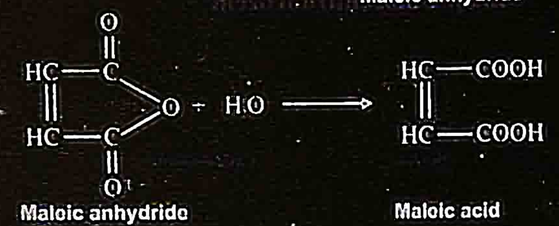
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- **Combustion:**



- **Catalytic Oxidation:**

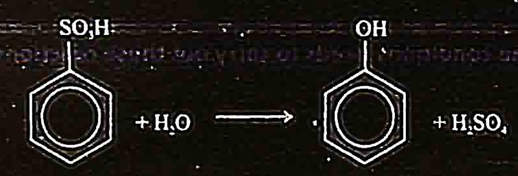




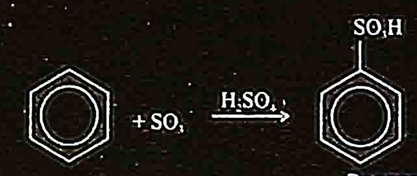
(iii)



(iv)



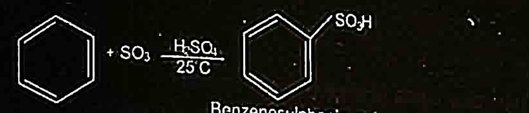
(v)

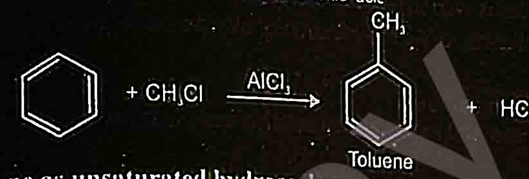


Q14. Detail out three reactions in which benzene behaves as if it is a saturated hydrocarbon and three reactions in which it behaves as if it is unsaturated.

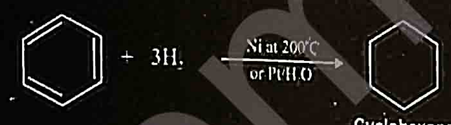
Ans. Benzene as saturated hydrocarbon:

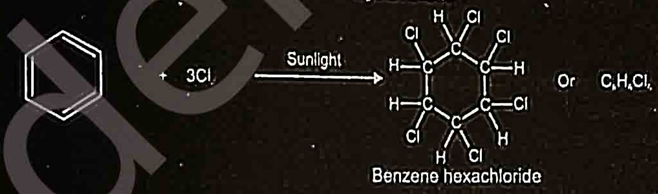


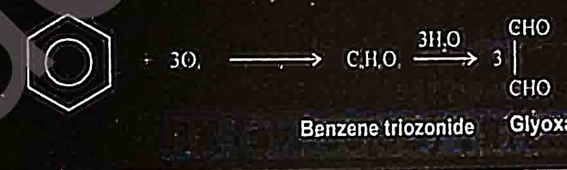




Benzene as unsaturated hydrocarbon:





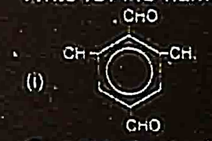


Previous Board Questions

1. What happens when a mixture of benzene vapours and air are passed over heated vanadium pentaoxide? Give equation.
2. Write mechanism of Alkylation of Benzene.
3. How will you prepare m-dinitrobenzene from benzene in two steps? Give equations.
4. What are the two main classes of aromatic compounds? Give their examples.
5. Write down two reactions showing that benzene is an unsaturated compound.
6. Prepare m-nitrotoluene from benzene.
7. Make two Isomers of Xylene and write their IUPAC names.
8. Chlorination of nitrobenzene in presence of $FeCl_3$, yields meta-chloro nitrobenzene as the main product. Why?
9. Give two reactions which show that benzene is a saturated compound.
10. What information are obtained by the x-rays analysis of benzene?
11. Write equations for the preparation of following form benzene
    (a) Maleic anhydride (b) Glyoxal
12. Write two rules for second substitution in benzene.
13. Convert ethylbenzene into benzoic acid.
14. Draw structural formula of triphenyl methane and benzotrichloride.
15. Ortho para directing groups increase reactivity of benzene, why?
16. Nitro group when present on the benzene ring acts as meta directing, why?

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17. How benzene is obtained from
    (a) Acetylene (b) n-hexane
18. Give three examples of condensed aromatic hydrocarbons and give their names?
19. What are the major products when chlorine reacts with toluene in the presence of sunlight?
20. Nitration of toluene gives ortho and p – nitrotoluene, while the nitration of nitrobenzene gives metadinitrobenzene. Give reasons?
21. Give four examples of aromatic heterocyclic compounds.
22. Write down the resonance structures of benzene and indicate their relative contributions towards the actual structure of benzene.
23. How does ozone affect benzene to give glyoxal?
24. Confirm by two reactions the presence of three alternate double bonds in benzene.
25. How nitration of benzene takes place? Give its mechanism.
26. Write IUPAC names of

(i) 

(ii) 

27. Give the mechanism of Friedel-Crafts acylation reaction.
28. What is meant by the term sulphonation?
29. What are polycyclic aromatic hydrocarbons?
30. Why Benzene give a cyclic structure?
31. What happens when benzene is burnt in free supply of air?

For Answers see
Scholar's CHEMISTRY (Objective) XII
AVAILABLE IN MARKET BY THE SAME AUTHORS
Mcq's, Additional Short Questions with Answers
Previous Board papers
With NTRY TESTS MCQ's
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CHAPTER 10

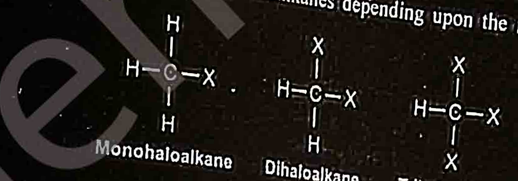
ALKYL HALIDES

Introduction

Haloalkanes

Halogen derivatives of alkanes are called haloalkanes.

They may be mono, di, tri or poly haloalkanes depending upon the number of halogen atoms present in the molecule.



Alkyl halides do not exist in nature. They are synthetic compounds and have olly nature.

Alkyl Halides

Monohaloalkanes are called alkyl halides or haloalkanes containing one halogen atom are called alkyl halides.

Their general formula is R – X, where R may be methyl, ethyl, propyl, etc. and X represents halogen atom (F, Cl, Br, I).

Classification of Alkyl Halides

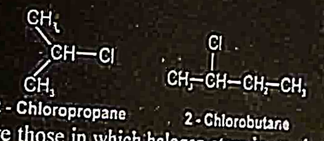
Mono haloalkanes or alkyl halides are further classified into primary, secondary and tertiary alkyl halides depending upon the type of carbon atom bearing the halogen atom.

(i) **Primary alkyl halides** are those in which halogen atom is attached with a carbon atom which is further attached to one or no carbon atom.

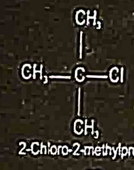
Examples: $CH_3 - Cl$ Chloromethane; $CH_3 - CH_2 - Cl$ Chloroethane; $CH_3 - CH_2 - CH_2 - Cl$ 1-Choropropane

(ii) **Secondary alkyl halides** are those in which halogen atom is attached with a carbon atom which is further attached to two other carbon atoms directly.

Examples:



(iii) **Tertiary alkyl halides** are those in which halogen atom is attached to a carbon atom which is further attached to three carbon atoms directly.

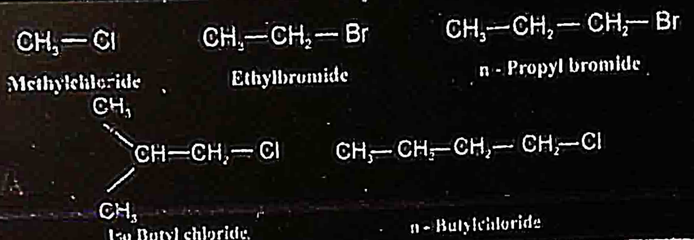


Nomenclature of Alkyl Halides

(a) Common Names

Alkyl halides (monohaloalkanes) are named according to the nature of the alkyl group to which halogen atom is attached. For example,

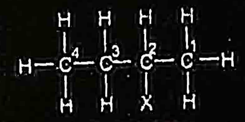
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(b) IUPAC Nomenclature

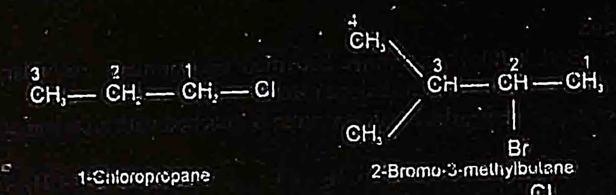
The systematic names given to alkyl halides follow the underlying rules.

1. Select the longest continuous carbon chain and consider the compound to have been derived from this structure.
2. Number the carbon atoms in the chain so that the carbon atom bearing the functional group (F, Cl, Br, I) gets the lowest possible number, e.g.,

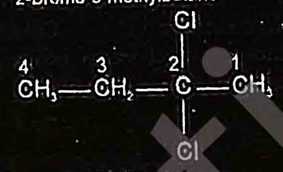


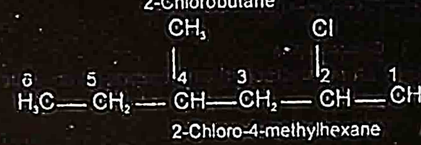
3. If the same alkyl substituent occurs more than once on the chain, the prefix di, tri, and so on are used before the name of the alkyl group.
4. The positions of the substituents are indicated by the appropriate numbers separated by commas.
5. If the same substituent occurs twice or more on the same carbon atom the number is repeated.

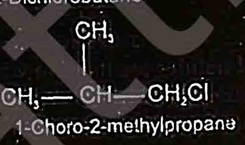
Examples.

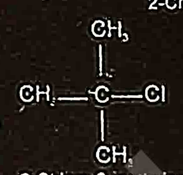


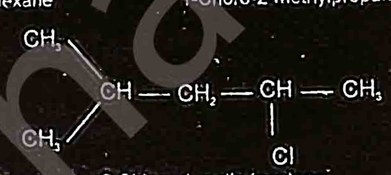


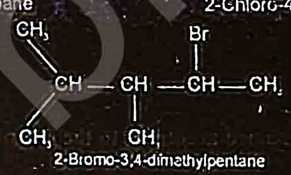










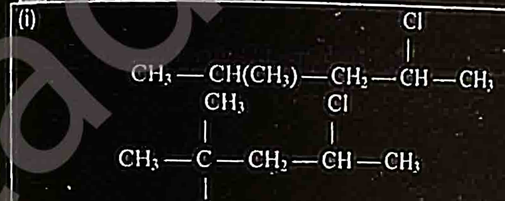


Q6. Give IUPAC names to the following compounds.

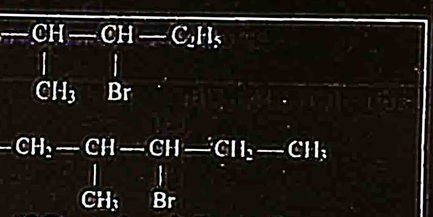
(i) $CH_3 - CH(CH_3) - CH_2 - CH(Cl) - CH_3$	(ii) $C_2H_5 - CH(CH_3) - CH(Br) - C_2H_5$
(iii) $(C_2H_5)_2CH - CH_2 - CH(Cl) - CH_3$	(iv) $(CH_3)_3C - CH_2 - Cl$
(v) $(CH_3)_2CHBr$	(vi) $(CH_3)_2CH-CH_2-CH(C_2H_5)CH_2Cl$
(vii) CBr_4	(viii) $H_2C(Br) - CH_2(Br)$
(ix) CH_2Cl_2	(x) $(CH_3)_3C-CH_2-CH_2-Br$
(xii) $(CH_3)_2C(Cl) - C(Cl)(CH_3)_2$	(xi) $(CH_3)_2CH - CH_2 - C(Cl)(CH_3)_2$
(xiv) $(CH_3CH_2)_3CBr$	

Ans

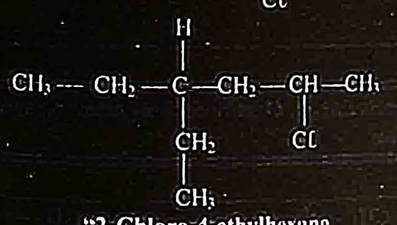
(i)



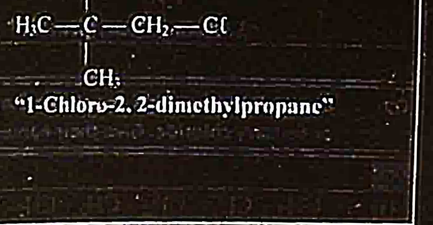
(ii)



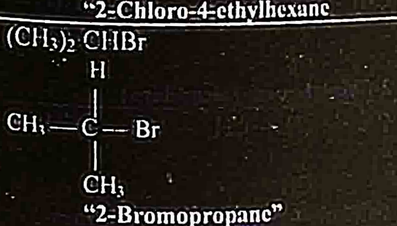
(iii)



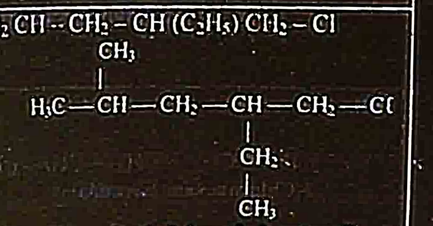
(iv)



(v)

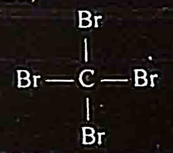


(vi)



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(vii) CBr_4

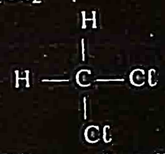


"Tetrabromomethane"

(viii) H_2C-CH_2 (Br, Br)

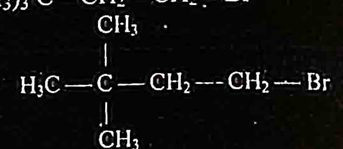
"1, 2-Dibromoethane"

(ix) CH_2Cl_2



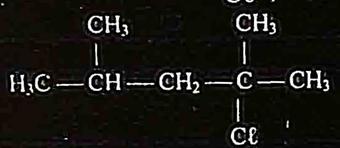
"Dichloromethane"

(x) $(CH_3)_3C-CH_2-CH_2-Br$



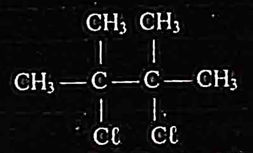
"1-Bromo-3, 3-dimethylbutane"

(xi) $(CH_3)_2CH-CH_2-C(CH_3)_2$ (Cl)



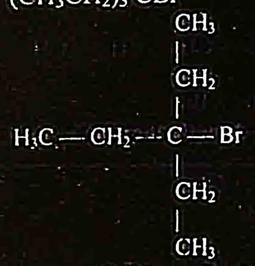
"2-Chloro-2, 4-dimethylpentane"

(xii) $(CH_3)_2C(Cl)-C(Cl)(CH_3)_2$



"2, 3-Dichloro-2, 3-dimethylbutane"

(xiii) $(CH_3CH_2)_3CBr$



"3-Bromo-3-ethylpentane"

Q7. Draw all the possible structures that have the molecular formula $C_6H_{13}Cl$, Classify each as primary, secondary or tertiary chloride. Give their names according to IUPAC system.

Ans

(i) $CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-Cl$

1-Chlorohexane (primary)

(ii) $CH_3-CH(Cl)-CH_2-CH_2-CH_2-CH_3$

2-Chlorohexane (secondary)

(iii) $CH_3-CH_2-CH_2-CH(Cl)-CH_2-CH_3$

3-Chlorohexane (secondary)

(iv) $CH_3-CH(CH_3)-CH_2-CH_2-CH_2-Cl$

1-Chloro-4-methylpentane (primary)

(v) $CH_3-CH(CH_3)-CH_2-CH(Cl)-CH_3$

2-Chloro-4-methylpentane (secondary)

(vi) $CH_3-CH(CH_3)-CH(Cl)-CH_2-CH_3$

3-Chloro-2-methylpentane (secondary)

(vii) $CH_3-CH(Cl)(CH_3)-CH_2-CH_3$

2-Chloro-2-methylpentane (tertiary)

(viii) $Cl-CH_2-CH(CH_3)-CH_2-CH_3$

1-Chloro-2-methylpentane (primary)

(ix) $CH_3-CH_2-CH(CH_3)-CH_2-CH_2-Cl$

1-Chloro-3-methylpentane (primary)

(x) $CH_3-CH_2-CH(CH_3)-CH(Cl)-CH_3$

2-Chloro-3-methylpentane (secondary)

(xi) $CH_3-CH_2-C(CH_3)(Cl)-CH_2-CH_3$

3-Chloro-3-methylpentane (tertiary)

(xii) $CH_3-C(CH_3)_2-CH_2-Cl$

1-Chloro-3, 3-dimethylbutane (primary)

(xiii) $CH_3-C(CH_3)_2-CH(Cl)-CH_3$

2-Chloro-3, 3-dimethylbutane (secondary)

(xiv) $CH_3-CH_2-C(CH_3)_2-CH_2-Cl$

1-Chloro-2, 2-dimethylbutane (primary)

(xv) $CH_3-CH(CH_3)-CH(Cl)-CH_3$

1-Chloro-2, 3-dimethylbutane (primary)

(xvi) $CH_3-CH(CH_3)-C(Cl)(CH_3)-CH_3$

2-Chloro-2, 3-dimethylbutane (tertiary)

(xvii) $CH_3-CH_2-CH(CH_2Cl)-CH_2-CH_3$

1-Chloro-2-ethylbutane (primary)

Q. 4. Which are the best methods of preparing alkyl Halides?

Methods of Preparation of Alkyl Halides

Alkyl halides can be prepared by the halogenation of alkanes and by the addition of halogen acids to alkenes.

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(i) $CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$

(ii) $CH_2=CH_2 + HCl \longrightarrow CH_3-CH_2-Cl$

Q. 4. Which is the best method of preparing alkyl Halides?

The best methods for the preparation of alkyl halides is from alcohols.

1. From Alcohols

(a) Reactions of alcohols with halogen acids:

Alcohols may be converted to the corresponding alkyl halides by the action of halogen acid in the presence of $ZnCl_2$ which acts as a catalyst (Lucas reagent).

$$CH_3CH_2-OH + HX \xrightarrow{ZnCl_2} \underset{\text{Ethyl halide}}{CH_3CH_2-X} + H_2O$$

$$CH_3CH_2-OH + HCl \xrightarrow{ZnCl_2} \underset{\text{Ethyl chloride}}{CH_3CH_2-Cl} + H_2O$$

(b) Reactions of alcohols with Thionyl Chloride (Darzen's Method):

Alcohols react with thionyl chloride in pyridine as a solvent to give alkyl chlorides.

$$ROH + SOCl_2 \xrightarrow{\text{Pyridine}} R-Cl + SO_2 + HCl$$

$$CH_3CH_2-OH + SOCl_2 \xrightarrow{\text{Pyridine}} \underset{\text{Ethyl chloride}}{CH_3CH_2-Cl} + SO_2 + HCl$$

- Pyridine acts as a base and remove HCl.
- This method is especially useful since the by-products (HCl, SO_2) are gases, which escape leaving behind the pure product.

Lucas' reagent is a solution of zinc chloride in concentrated hydrochloric acid. This solution is used to distinguish alcohols.

(c) Reactions of alcohols with PBr_3 and PCl_5:

Phosphorus trihalides or phosphorus pentahalides react with alcohols to replace -OH group by a halo group.

$$3CH_3-CH_2-OH + PBr_3 \longrightarrow 3CH_3-CH_2-Br + H_3PO_3$$

$$CH_3-CH_2-OH + PCl_5 \longrightarrow CH_3-CH_2-Cl + POCl_3 + HCl$$

2. Halogen Exchange Method

An excellent method for the preparation of simple alkyl iodide is the treatment of alkyl chloride or alkyl bromide with sodium iodide. This method is particularly useful because alkyl iodides cannot be prepared by the direct iodination of alkanes.

$$RCl + NaI \longrightarrow RI + NaCl$$

$$RBr + NaI \longrightarrow RI + NaBr$$

Reactivity of Alkyl Halides

An alkyl halide molecule (R—X) consists of two parts, An alkyl group with a partial positive charge on the carbon atom attached to a halogen atom and the halide atom with a partial negative charge.

There are two main factors which govern the reactivity of R—X bond. These are:

(i) C—X Bond energy

(ii) C—X Bond polarity

Bond Energy

Smaller the bond energy, greater will be the reactivity of a bond and vice versa. The strength of the bonds show that iodo compounds (with the weakest bonds) would be the most reactive one while fluoro compounds will be the least reactive. So the order of reactivity of alkyl halides should be

R— I > R—Br > R— Cl > R— F

Bond	Bond Energy (kJ/mole)
C—F	467
C—H	413
C—Cl	346
C—Br	290
C—I	228

Atom	Electro-negativity
F	4.0
Cl	3.0
Br	2.8
I	2.5
C	2.5
H	2.1

Bond Polarity

A polar bond is more reactive than a non-polar bond. The greatest electronegativity difference exists between carbon and fluorine atoms in alkyl fluorides. If an electrophile is the attacking reagent then this difference suggests that alkyl fluorides would be the most reactive one. On the same lines, alkyl iodides should be the least reactive alkyl halides.

Conclusion:

In the light of the above discussion, it is clear that the two factors mentioned above predict different types of behaviour about the reactivity of alkyl halides.

Experiments have shown that the strength of carbon halogen bond is the main factor which decides the reactivity of alkyl halides.

So the overall order of reactivity of alkyl halides for a particular alkyl group is:

Iodide > Bromide > Chloride > Fluoride

In fact the C–F bond is so strong that alkyl fluorides do not react under ordinary conditions.

Reactions of Alkyl Halides

The reactions of alkyl halides fall into two categories.

1. Those reactions in which the halogen is replaced by some other atom or a group (nucleophilic substitution, or S_N reactions).
2. Those which involve the removal of HX from the halide (elimination, or E-reactions).

Nucleophilic Substitution Reactions

General Pattern of S_N Reactions:

The overall process describing a S_N reaction is shown as follows:

$$Nu^- + -\overset{|}{C}-L \longrightarrow Nu-\overset{|}{C}- + L^-$$

In this equation the incoming group Nu^- is a nucleophile and "L" is leaving group.

Nucleophile

- Nucleophile means nucleus loving.
- It has an unshared electron pair available for bonding.
- In most cases it is basic in character.
- It may be negatively charged or neutral.

Examples of Nucleophiles

HO^-	Hydroxide ion	Cl^-	Chloride ion
$C_2H_5O^-$	Ethoxide ion	Br^-	Bromide ion
H_2S^-	Hydrogen sulphide ion	NH_3	Ammonia
SCN^-	Thiocyanate ion	CN^-	Cyanide ion
$H_2\ddot{O}:$	Water	I^-	Iodide ion
NH_2^-	Amino group		

Electrophile

- It is a specie which attracts electrons (electron loving).
- In most cases, it is acidic in character.
- The carbon atom of an alkyl group attached with the halogen atom and bearing a partial positive charge is called an electrophile or electrophilic center.
- An electrophile may be neutral or positively charged.

Examples: $AlCl_3$, BF_3, NH_4^+, Cl^+, Br^+, NO_2^+, SO_3, R^+ etc.

Leaving Group (L)

- Leaving group (L) is also a nucleopile.
- It is called leaving group because it departs with an unshared pair of electrons.
- If we wish a S_N reaction to proceed in the forward direction the incoming nucleophile must be stronger than the departing one.

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Good Leaving Groups	Poor Leaving Groups	Good Leaving Group & Good nucleophile
Cl^-, Br^-, I^-, HSO_4^-	OH^-, OR^-, NH_2^-	I^- (Iodide Ion)

Iodide ion is a good nucleophile because of high polarizability and a good leaving group because of low bond energy.

Substrate Molecule

The alkyl halide molecule on which a nucleophile attacks is called a substrate molecule.

Q.9 Write a detailed note on mechanism of nucleophilic substitution reactions.

Mechanism of Nucelophilic Substitution Reactions

Alkyl halides may undergo nucleophilic substitution reactions in two different ways:

1. Nucleophilic Substitution Bimolecular (S_N2)
2. Nucleophilic Substitution Unimolecular (S_N1)

Nucleophilic substitution reactions on alkyl halides involve two main processes, the breakage of C – X bond and the formation of C – Nu bond. The mechanism of the nucleophilic substitution reactions depends upon the timing of these two processes. If the two processes occur simultaneously the mechanism is called S_N2. If the bond breaks first followed by the formation of a new bond, the mechanism is called S_N1.

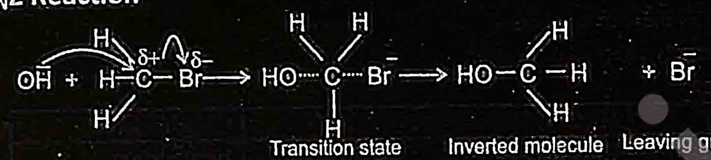
Nucleophilic Substitution Bimolecular (S_N2)

Definition

"The nucleophilic substitution reaction mechanism in which breaking of C – X bond and the formation of C – Nu bond occur simultaneously in one step is called S_N2 reaction."

Example: $C_2H_5Br + KOH_{(aq)} \longrightarrow C_2H_5OH + KBr$

Mechanism of S_N2 Reaction



Explanation

Single step Reaction

This is a single step mechanism. As soon as the nucleophile starts attaching the electrophilic carbon of the substrate, the bond with which the leaving group is attached, starts breaking. In other words the extent of bond formation is equal to the extent of bond breakage.

Direction of Attack

The attacking nucleophile attacks from the side which is opposite to the leaving group.

Change in Hybridization

In order to give to the nucleophile enough room to attack, the substrate carbon atom changes its state of hybridization from tetrahedral sp^3 to planar sp^2. The attack of the nucleophile, the change in the state of hybridization and the departure of the leaving group everything occurs at the same time.

Inversion of Configuration

During the reaction the configuration of the alkyl halide molecule gets inverted. There is 100% inversion of configuration.

Molecularity

Number of molecules taking part in the rate determining step is called molecularity. Since in this mechanism, the reaction takes place in only one step which is also a rate determining step and two molecules are participating in this step, so it is called a bimolecular reaction.

Reaction Kinetics

Kinetic studies of the reactions involving S_N2 mechanism have shown that the rates of such reactions depend upon the concentrations of alkyl halide as well as the attacking nucleophile. Mathematically, the rate can be expressed as:

Rate = k [substrate] [attacking nucleophile]

Nature of Alkyl Halides

Among the alkyl halides, the primary alkyl halides always follow S_N2 mechanism whenever they are attacked by nucleophiles.

Nucleophilic Substitution Unimolecular (S_N1)

Definition

"The nucleophilic substitution reaction mechanism in which breaking of C – X bond and the formation of C – Nu bond occur one after the other in two different steps is called S_N1 reaction."

Example: $(CH_3)_3C{-}Cl + KOH_{(aq)} \longrightarrow (CH_3)_3C{-}OH + KCl$

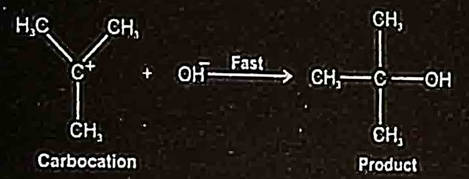
Mechanism of S_N1 Reaction

First Step:



MCQ
Rate of S_N1 reaction is not effected by:
a) Nature of solvent
b) Stability of carbocation
c) Nature of leaving group
d) Conc. of nucleophile
e) Conc. of alkyl halides

Second Step:



Stability order of Carbocations.
T° carbocation > S° carbocation > P° carbocation

Explanation

Two Steps Reaction

It is a two steps mechanism. The first step is the reversible ionization of the alkyl halide in the presence of an aqueous acetone or an aqueous ethyl alcohol. This step provides a carbocation as an intermediate. In the second step this carbocation is attacked by the nucleophile to give the product.

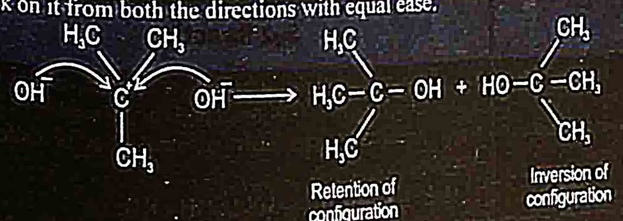
Since the first step involves the breakage of a covalent bond so it is a slow step as compared to the second step which involves the energetically favourable combination of ions. The first step is therefore, called the rate–determining step.

Molecularity

The mechanism is called unimolecular (molecularity is one) because only one molecule takes part in the rate determining step.

Direction of Attack

In S_N1 mechanism, the nucleophile attacks when the leaving group had already gone, so the question of the direction of the attack does not arise. Moreover, the intermediate carbocation is planer specie allowing the nucleophile to attack on it from both the directions with equal ease.



MCQ's

The final product obtained when NH_3 is treated with excess of ethyl bromide
(a) Ethylamine
(b) Diethylamine
(c) Triethylamine
(d) Quaternary ethylammonum

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Configuration of Product

There is 50% inversion of configuration and 50% retention of configuration.

Reaction Kinetics

Reactions involving S_N1 mechanism show first order kinetics and the rates of such reactions depend only upon the concentration of the alkyl halide. The rate equation of such reactions can be written as follows:

$$\text{Rate} = k\,[\text{Alkyl halide}]$$

Nature of Alkyl Halides

Tertiary alkyl halides when attacked by a nucleophile always follow S_N1 mechanism.

Note: In all secondary alkyl halides S_N reaction may occur through S_N1 mechanism or S_N2 mechanism depending on the nature of the solvent in which the reaction is carried out. Polar solvents help in ionization so they favour S_N1 Reactions.

Examples of S_N Reactions

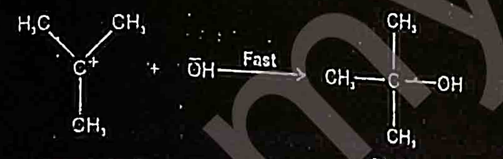
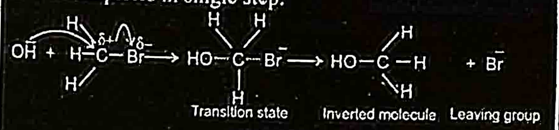
Some S_N reactions are given below:

Substrate		Attacking Nucleophile		Product		
$CH_3\overset{\delta+}{C}H_2—Br^{\delta-}$	+	$\bar{O}H$	⟶	C_2H_5OH Ethylalcohol	+	Br^-
$CH_3\overset{\delta+}{C}H_2—Br^{\delta-}$	+	I^-	⟶	C_2H_5I Ethyliodide	+	Br^-
$CH_3\overset{\delta+}{C}H_2—Br^{\delta-}$	+	CN^-	⟶	C_2H_5CN Propanenitrile	+	Br^-
$CH_3\overset{\delta+}{C}H_2—Br^{\delta-}$	+	$N\bar{O}_2$	⟶	$C_2H_5NO_2$ Nitroethane	+	Br^-
$CH_3\overset{\delta+}{C}H_2—Br^{\delta-}$	+	CH_3O^-	⟶	$CH_3—CH_2—O—CH_3$ Ethylmethylether	+	Br^-
$CH_3\overset{\delta+}{C}H_2—Br^{\delta-}$	+	$\ddot{N}H_3$	⟶	$C_2H_5—NH_2$ Ethylamine	+	HBr
$CH_3\overset{\delta+}{C}H_2—Br^{\delta-}$ + $CH_3—CH_2—\ddot{N}H_2$			⟶	$(CH_3—CH_2)_2NH$ Diethylamine	+	HBr
$CH_3\overset{\delta+}{C}H_2—Br^{\delta-}$ + $(CH_3—CH_2)_2\ddot{N}H$			⟶	$(CH_3—CH_2)_3N$ Triethylamine	+	HBr
$CH_3\overset{\delta+}{C}H_2—Br^{\delta-}$ + $(CH_3—CH_2)_3\ddot{N}$			⟶	$(CH_3—CH_2)_4N^+$ Quaternary ethylammonium ion.	+	Br^-
$CH_3\overset{\delta+}{C}H_2—Br^{\delta-}$ +		$\bar{S}H$	⟶	C_2H_5SH Ethyl thioalcohol	+	Br^-
$CH_3\overset{\delta+}{C}H_2—Br^{\delta-}$ +		$CH_3COO^-Na^+$	⟶	$CH_3COOC_2H_5$ Ethyl acetate	+	NaBr

Q. How do you differentiate between S_N1 and S_N2 mechanism.

Ans.

S_N1 Reaction	S_N2 Reaction
1. "The nucleophilic substitution reaction mechanism in which breaking of C – X bond and the formation of C – Nu bond occur one after the other in two different steps is called S_N1 reaction." $(CH_3)_3C—Cl + KOH_{(aq)} \longrightarrow (CH_3)_3C—OH + KCl$	1. "The nucleophilic substitution reaction mechanism in which breaking of C – X bond and the formation of C – Nu bond occur simultaneously in one step is called S_N2 reaction." $C_2H_5Br + KOH_{(aq)} \longrightarrow C_2H_5OH + KBr$

2. It completes in two steps. **First Step:**  **Second Step:** 	2. It completes in single step. 
3. The attacking nucleophile can attack from either side.	3. The attacking nucleophile attacks from opposite side of the leaving group.
4. There is 50% inversion of configuration and 50% retention of configuration.	4. There is 100% inversion of configuration from alkyl halide into the product molecule.
5. Since one molecule takes part in rate determining step, so its molecularity is one (unimolecular)	5. Since two molecules i.e. substrate and attacking nucleophile take part in rate determining step, so its molecularity is two (bimolecular)
6. Kinetic study of reaction shows 1st order reaction. Rate = k [Alkyl halide]	6. Kinetic study of reaction shows 2nd order reaction. Rate = k [substrate] [attacking nucleophile]
7. Tertiary alkyl halides when attacked by a nucleophile always follow S_N1 mechanism.	7. Usually primary alkyl halides show or follow S_N2 mechanism depending upon their structure and the nature of the solvent.

Q. 10 What do you understand by the term β-elimination reaction? Explain briefly the two possible mechanism of β-elimination reaction.

β-Elimination Reactions

"Reactions of alkyl halides which involve the loss of two atoms or groups from the adjacent carbon atoms to give alkenes are called β-elimination reaction".

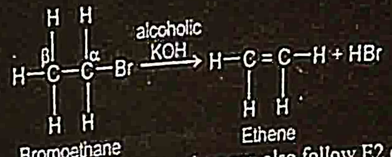
Explanation

During nucleophilic substitution reactions, the attacking nucleophile attacks the electrophilic carbon atom of the alkyl halide. There is another site present in the alkyl halide molecule where the nucleophile can attack at the same time. Such a site is an electrophilic hydrogen atom attached to the β–carbon of the alkyl halide. When the attack takes place on hydrogen, we get an alkene instead of a substitution product. Such a type of reactions are called elimination reactions. Such a site is an electrophilic hydrogen atom attached to the β–carbon of the alkyl halide. When the attack takes place on hydrogen, we get an alkene instead of a substitution product. Such a type of reactions are called elimination reactions. These reactions take place simultaneously with substitution reactions and often compete with them.

Types of Elimination Reactions

β–elimination reactions are of two types:

(i) E2 reactions
(ii) E1 reactions

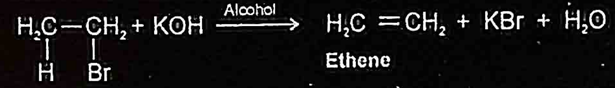


Like nucleophilic substitutions, the elimination reactions can also follow E2 or E1 mechanism.

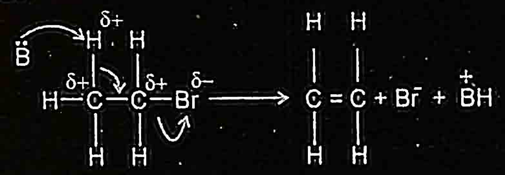
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(i) E2 Reaction

"One step elimination reaction in which both the atoms or groups leave simultaneously is called E2 reaction".



Mechanism of E2 Reaction



Single Step Reaction

Single step reaction which is slow and rate determining step with the rate transition state. In the same step, base attacks on the acidic hydrogen and halogen atom is removed simultaneously resulting in alkene formation.

Molecularity

Bimolecular reaction as two molecules are taking part in the rate determining step.

Reaction Kinetics

Rate = k[alkyl halide] [base]

Chemical kinetics shows that it is 2nd order reaction.

Nature of Alkyl Halides

Usually primary alkyl halides follow E2–mechanism.

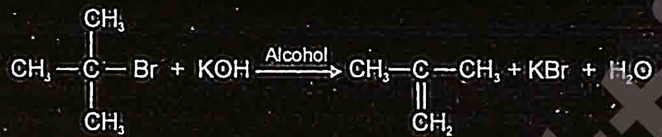
Factors effecting E2 Reaction

The rate of those reactions which follow E2 mechanism depend upon the concentrations of the alkyl halide as well as the attacking nucleophile or a base.

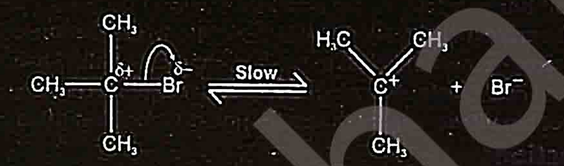
- It competes S_N2 reaction.

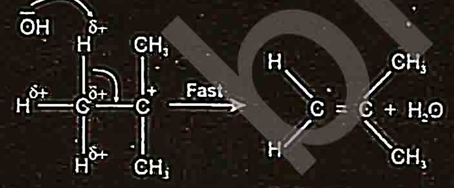
(ii) E1 Reaction

"Two steps elimination reaction in which the leaving group leaves first followed by the removal of hydrogen is called E1 reaction".



Mechanism of E1 Reaction





Two Steps Reaction

The first step is slow, reversible and carbocation is formed. In the second step the base (sometimes solvent) removes acidic hydrogen and alkenes is formed.

Molecularity

It is unimolecular reaction.

Reaction Kinetics

Rate = k[alkyl halide]

Chemical kinetics shows that it is 1st order reaction.

Nature of Alkyl Halides

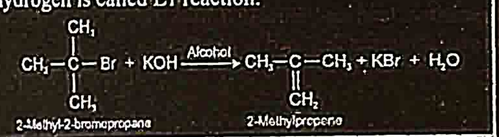
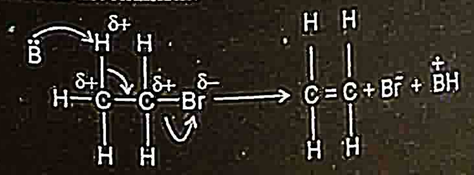
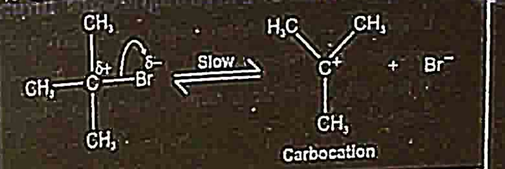
Generally tertiary alkyl halides show E1 reactions

Factors effecting E_1 Reaction

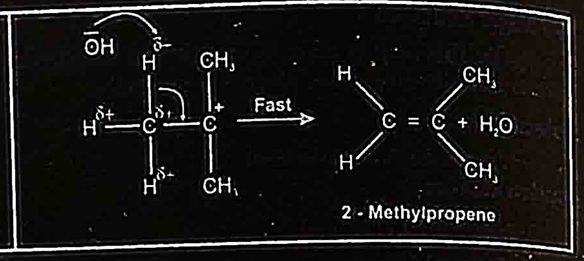
The rates of those reactions which follow E1 mechanism depend only upon the concentration of the alkyl halide molecule.

- It competes S_N1 reaction.

Q. Differentiate between E1 and E2 reactions.

E2 REACTION	E1 REACTION
One step elimination reaction in which both the atoms or groups leave simultaneously is called E2 reaction. 	Two steps elimination reaction in which the leaving group leaves first followed by the removal of hydrogen is called E1 reaction. 
1. Bimolecular reaction as two molecules are taking part in the rate determining step.	1. It is unimolecular reaction.
2. Single step reaction which is slow and rate determining step with the rate transition state. In the same step, base attacks on the acidic hydrogen and halogen atom is removed simultaneously resulting in alkene formation.	2. Two step reaction. The first step is slow, reversible and carbocation is formed. In the second step the base (sometimes solvent) removes acidic hydrogen and alkene is formed.
3. Rate = k[alkyl halide] [base]	3. Rate = k[alkyl halide]
4. Chemical kinetics shows that it is 2nd order reaction.	4. Chemical kinetics shows that it is 1st order reaction.
5. Usually primary alkyl halides follow E2–mechanism.	5. Usually tertiary alkyl halides show E1 mechanism.
6. It competes S_N2 reaction.	6. It competes S_N1 reaction.
7. General mechanism. 	7. General mechanism. 

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Other reactions of Alkyl halides

(1) Wurtz Synthesis

Alkyl halides react with sodium in dry ether solvent to give alkanes. The reaction is particularly useful for the preparation of symmetrical alkanes.

$$CH_3-CH_2-Cl + 2Na + Cl-CH_2-CH_3 \xrightarrow{\text{Ether}} \underset{\text{n - Butane}}{CH_3-CH_2-CH_2-CH_3} + 2NaCl$$

(2) Reduction of Alkyl Halides

Alkyl halides can be reduced with zinc in the presence of an aqueous acid such as HCl or CH_3COOH.

$$CH_3-CH_2-CH_2-Cl + Zn + H^+ + Cl^- \longrightarrow \underset{\text{Propane}}{CH_3-CH_2-CH_3} + ZnCl_2$$

(3) Reaction with Sodium Lead Alloy (Na_4Pb)

Methyl chloride and ethyl chloride react with sodium lead alloy giving tetramethyl lead and tetraethyl lead, respectively. These compounds are important anti-knock agents and are used in gasoline.

$$4CH_3Cl + Na_4Pb \longrightarrow \underset{\text{Tetramethyl lead}}{(CH_3)_4Pb} + 4NaCl$$

$$4CH_3CH_2Cl + Na_4Pb \longrightarrow \underset{\text{Tetraethyl lead (TEL)}}{(CH_3CH_2)_4Pb} + 4NaCl$$

MCQ's

Which of the following product is formed when ethyl chloride is treated with Na in ether?

(a) n–Butane (b) Propane
(c) Ethane (d) Methane
(e) All of these

Grignard Reagent

- Grignard reagents RMgX are derivatives of alkyl halides belonging to class of organo-metallic compounds.
- Grignard reagent was first prepared by Victor Grignard in 1900.
- These reagents are so important in organic synthesis that almost all the classes of organic compounds can be prepared from them.
- Due to their importance and applications Victor Grignard was awarded Nobel Prize in chemistry.

Organometallic Compounds:

These are compounds in which metal atom is directly bonded to carbon atom of organic part. e.g.,

n–butyllithium, Diethylzinc, Grignard reagents etc.

Q.5 Write down a method for the preparation of ethyl magnesium bromide in the laboratory?

Ans

Preparation of ethylmagnesium bromide

Grignard reagents are prepared by the reaction of magnesium metal with alkyl halides in the presence of dry ether (alcohol free, moisture free). $R^{\delta+}-X^{\delta-} + Mg \xrightarrow{\text{Ether}} R-Mg-X$

When ethylbromide is treated with magnesium metal in the presence of dry ether, ethylmagnesium bromide is formed.

$$CH_3-CH_2-Br + Mg \xrightarrow{\text{Ether}} \underset{\text{Ethyl magnesium bromide}}{CH_3-CH_2-Mg-Br}$$

Caution: It is important that all the reactants must be absolutely dry and pure because Grignard reagents are so reactive that they may react with moisture or any impurity present.

Q. Why dry ether is necessary for the preparation of Grignard reagent?

Ans Grignard reagents are much reactive class of organic compounds. They immediately react with moisture or any impurity (alcoholic contents) and decomposed into alkanes. Therefore during the preparation of Grignard reagents all the reactants must be absolutely dry and pure.

$$R^{\delta+}-X^{\delta-} + Mg \xrightarrow{\text{Ether}} R-Mg-X$$

Order of Reactivity:

- Reactivity of alkyl halides with magnesium is in the following order:
  Alkyl iodide > Alkyl bromide > Alkyl chloride
- For a given halogen the order of reactivity is as follows:
  $CH_3X > C_2H_5X > C_3H_7X$

Q. Grignard reagents are so reactive organic compounds. Justify?

Ans Grignard reagents are much reactive than most of the organic compounds. The reactivity is due to the nature of C—Mg bond which is highly polar.

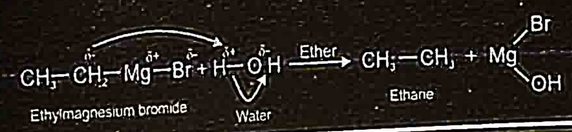
$$CH_3-H_2C^{\delta-}-Mg^{\delta+}-X^{\delta-}$$

Magnesium is more electropositive (E.N = 1.2) than carbon (E.N = 2.5) and the C—Mg bond though covalent is highly polar, giving alkyl carbon the partial negative charge. This negative charge is an unusual character which makes the alkyl groups highly reactive towards electrophilic centers.

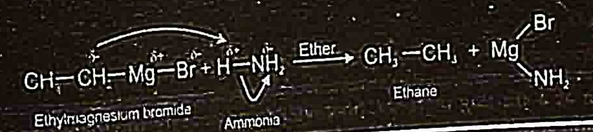
Mostly reactions shown by Grignard reagent are exothermic.

Reactions of Grignard Reagent

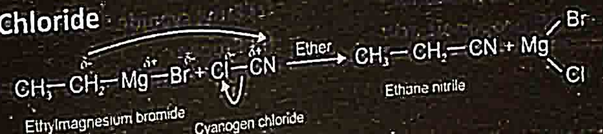
(i) With Water



(ii) With Ammonia



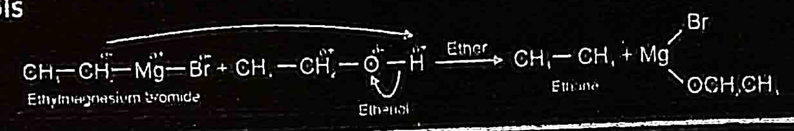
(iii) With Cyanogen Chloride



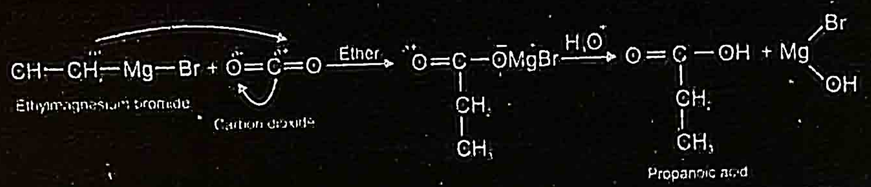
Alkane nitrile on hydrolysis gives carboxylic acid.

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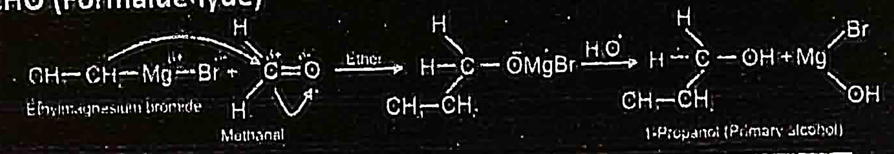
(iv) With Alcohols



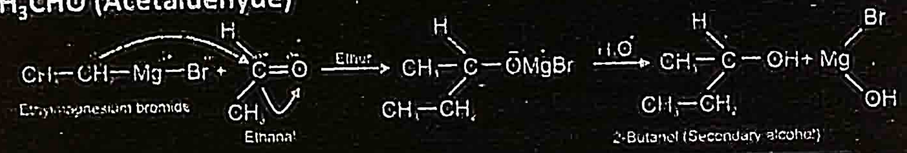
(v) With CO_2



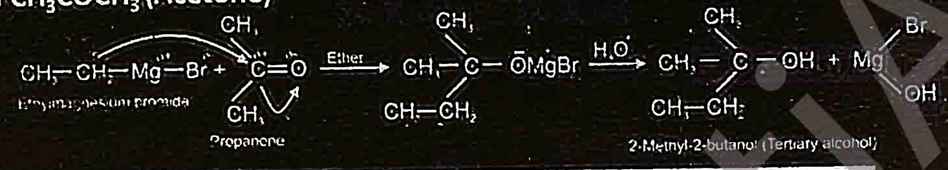
(vi) With HCHO (Formaldehyde)



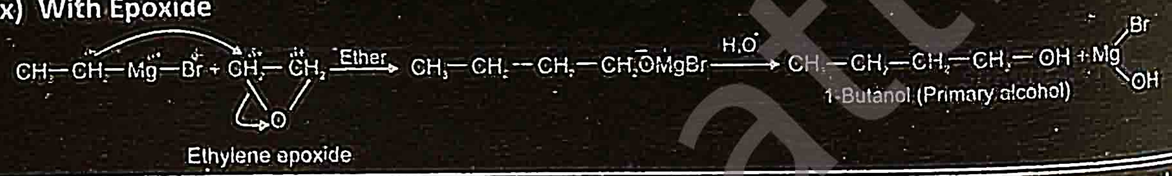
(vii) With CH_3CHO (Acetaldehyde)



(viii) With CH_3COCH_3 (Acetone)



(ix) With Epoxide



Q.8 Using ethyl bromide as a starting material, how would you prepare the following compounds? Give also the inorganic reagents and conditions necessary to carry out these reactions:

(a) n- Butane (b) Ethyl alcohol (c) Ethyl cyanide (d) Ethane
(e) Ethene (f) propanoic acid (g) Propane

Ans.

a) n-Butane:

$$C_2H_5-Br + 2Na + C_2H_5-Br \xrightarrow{\text{Ether}} H_3C-CH_2-CH_2-CH_3 + 2NaBr$$

n-Butane

b) Ethyl alcohol:

$$CH_3-\overset{\delta+}{C}H_2-\overset{\delta-}{B}r + NaOH_{(aq)} \rightarrow CH_3-CH_2-OH + NaBr$$

Ethyl alcohol

c) Ethyl cyanide:

$$CH_3-\overset{\delta+}{C}H_2-\overset{\delta-}{B}r + K-CN \rightarrow CH_3-CH_2-CN + KBr$$

Ethyl cyanide

d) Ethane: (Reduction)

$$CH_3-\overset{\delta+}{C}H_2-\overset{\delta-}{B}r + Zn + H^+ + Br^- \longrightarrow CH_3-CH_3 + ZnBr_2$$

Ethane

e) Ethene: (Dehydrohalogenation)

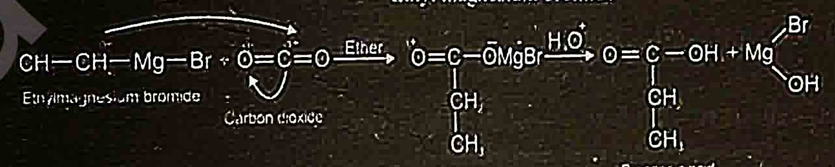
$$CH_3-\overset{\delta+}{C}H_2-\overset{\delta-}{B}r + KOH \xrightarrow[80\,^\circ C]{\text{Alcohol}} CH_2=CH_2 + H_2O + KBr$$

Ethene

f) Propanoic Acid:

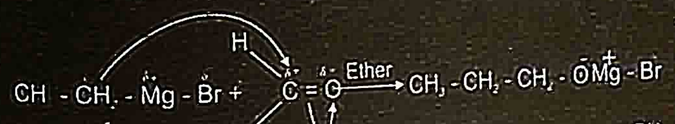
$$CH_3-CH_2-Br + Mg \xrightarrow{\text{Ether}} CH_3-\overset{\delta-}{C}H_2-\overset{\delta+}{M}g-\overset{\delta-}{B}r$$

Ethyl magnesium bromide



g) Propane:

$$CH_3-CH_2-Br + Mg \xrightarrow{\text{Ether}} CH_3-\overset{\delta-}{C}H_2-\overset{\delta+}{M}g-\overset{\delta-}{B}r$$



$$CH_3-CH_2-CH_2-O-Mg-Br \xrightarrow{H_3O^+} CH_3-CH_2-CH_2-OH + Mg(OH)Br$$

1-Propanol

$$CH_3-CH_2-CH_2-OH + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3-CH_2-CH_2-Cl + HCl + SO_2$$

$$CH_3-CH_2-CH_2-Cl + Zn + H^+ + Cl^- \longrightarrow CH_3-CH_2-CH_3 + ZnCl_2$$

Propane

Q12. How will you carry out the following conversions?

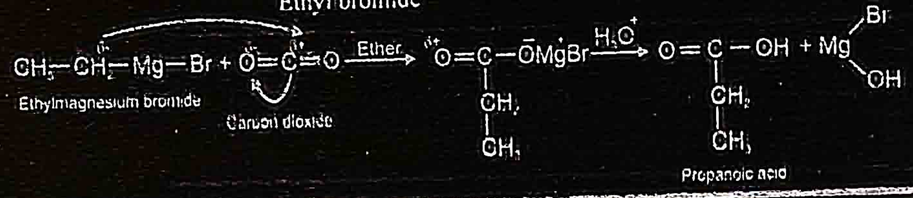
(i) $CH_4 \longrightarrow CH_3CH_2COOH$ (ii) $CH_3-CH_3 \longrightarrow (CH_3-CH_2)_4\,N^+Br^-$
(iii) $CH_2=CH_2 \longrightarrow CH_3-CH_2-CH_2-CH_2-OH$ (iv) $CH_3CH_2CH_2Cl \longrightarrow CH_3CH=CH_2$
(v) $CH_3COOH \longrightarrow CH_3CH_2COOH$

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Ans.

(i) $CH_4 \longrightarrow CH_3CH_2COOH$

- $CH_4 + Cl_2 \xrightarrow{\text{Sunlight}} CH_3Cl + HCl$
  methyl chloride
- $CH_3-CH_2Na+Cl-CH_3 \xrightarrow{\text{Ether}} CH_3-CH_3+2NaCl$
  Ethane
- $CH_3-CH_3+Br_2 \xrightarrow{\text{Sunlight}} CH_3-CH_2-Br+HBr$
  Ethyl bromide



(ii) $CH_3-CH_3 \rightarrow (CH_3-CH_2)_4N^+Br^-$

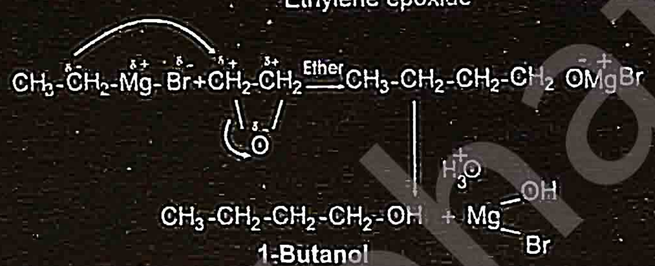
Ans.

- $CH_3-CH_3+Br_2 \xrightarrow{\text{Sunlight}} CH_3-CH_2-Br+HBr$
- $CH_3-CH_2-Br+NH_3 \longrightarrow CH_3-CH_2-NH_2+HBr$
  Ethylamine
- $CH_3-CH_2-Br+CH_3-CH_2-NH_2 \longrightarrow (CH_3-CH_2)_2NH+HBr$
  Diethylamine
- $CH_3-CH_2-Br+(CH_3-CH_2)_2NH \longrightarrow (CH_3-CH_2)_3N+HBr$
  Triethylamine
- $CH_3-CH_2-Br+(CH_3-CH_2)_3N \longrightarrow (CH_3-CH_2)_4N^+Br^-$
  Quarternary ethyl ammonium bromide

(iii) $CH_2=CH_2 \rightarrow$ 1-Butanol

Ans.

$$CH_2=CH_2+\tfrac{1}{2}O_2 \xrightarrow[300^\circ C]{Ag_2O} \underset{\text{Ethylene epoxide}}{\overset{CH_2-CH_2}{\diagdown O \diagup}}$$



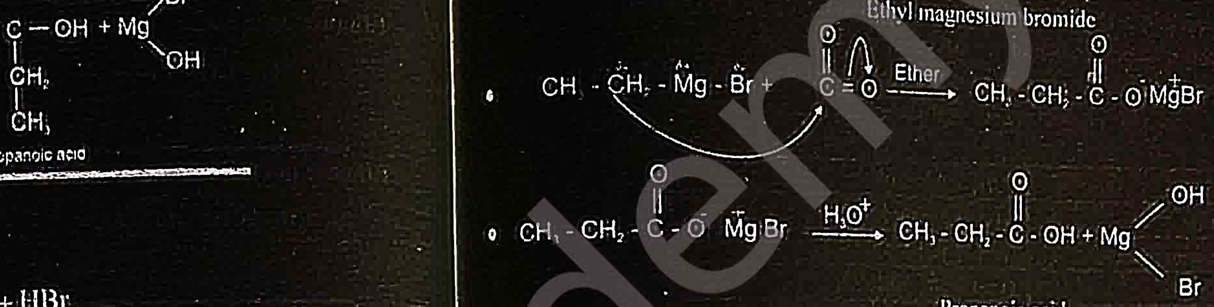
(iv) $CH_3-CH_2-CH_2-Cl \longrightarrow CH_3-CH=CH_2$

Ans. $CH_3-CH_2-CH_2-Cl+KOH \xrightarrow{\text{Alcohol}} CH_3-CH=CH_2+KCl+H_2O$
Propene

(v) $CH_3COOH \rightarrow CH_3CH_2COOH$

Ans.

- $CH_3COOH+NaOH \rightarrow CH_3COO^-Na^+ + H_2O$
  Sodium acetate
- $2CH_3COO^-Na^+ + 2H_2O \xrightarrow{\text{Electrolysis}} CH_3-CH_3 + 2NaOH + H_2 + 2CO_2$
  Ethane
- $CH_3-CH_3+Br_2 \xrightarrow{\text{Sunlight}} CH_3-CH_2-Br+HBr$
  Ethylbromide
- $CH_3-CH_2-Br+Mg \xrightarrow{\text{Ether}} CH_3-\overset{\delta-}{C}H_2-\overset{\delta+}{M}g-\overset{\delta-}{B}r$
  Ethyl magnesium bromide



KEY POINTS

1. Monohalo derivates of alkanes are called alkyl halides (RX).
2. The general formula of alkyl halides is $C_nH_{2n+1}X$.
3. The best method for the preparation of alkyl halides is by the reactions of alcohols with inorganic halides like $SOCl_2$, PX_3, and PX_5.
4. Alkyl halides are very reactive class of organic compounds. They undergo nucleophilic substitution reactions and elimination reactions in the presence of a nucleophile or a base.
5. Nucelophilic substitution reactions can take place in two distinct ways. A one step mechanism is called S_N2 while a two step mechanism is called S_N1. S_N1 reactions show first order kinetics whereas S_N2 reactions show 2^{nd} order kinetic.
6. Nucleophilic substitution reactions take place simultaneously with elimination reactions and often compete with them.
7. Elimination of two atoms or groups from adjacent carbon atoms in the presence of a nucleophile or a base is called elimination reaction. Like nucleophilic substitution. β – elimination reaction also take place in two distinct ways E2 and E1.
8. Grignard reagent can be prepared by adding alkyl halide in a stirred suspension of magnesium metal in diethyl ether.
9. Grignard reagent has a reactive nucleophilic carbon atom which can react with electrophilic centres to give the products in high yields.
10. Primary, secondary and tertiary alcohols can be best prepared by reacting Grignard reagent with formaldehyde, any other aldehydes and ketones, respectively.

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SOLVED OBJECTIVE EXERCISE

Q1. Fill in the blanks.

(i) In tertiary alkyl halides the halogen atom is attached to a carbon which is further attached to ____ carbon atoms directly.

(ii) The best method for the preparation of alkyl halides is the reaction of____ with inorganic reagents.

(iii) An alkyl group with a partial positive charge on the carbon atom is called _____ center.

(iv) The mechanism is called _____if it involves one molecule in the rate-determining step.

(v) The molecularity of a reaction is defined as the number of molecules taking part in the _____:

(vi) The molecularity of E2 reaction is always two and the reaction show _____order kinetics.

(vii) Wurtz synthesis is useful for the preparation of____ alkanes.

(viii) Grignard reagents are prepared by the reaction of magnesium metal with alkyl halides in the presence of ____

Answer Key.

(i)	Three	(ii)	Alcohols
(iii)	Electrophilic	(iv)	Unimolecular
(v)	Rate determining step	(vi)	Second
(vii)	Symmetrical	(viii)	Dry ether

Q2. Indicate True or false.

(i) In secondary alkyl halides, the halogen atom is attached to a carbon which is further attach to two carbon atoms directly.

(ii) Alcohols react with thionyl chloride in ether as solvent to give alky halides.

(iii) Order of reactivity of alky halides for a particular alkyl group is
Iodide > Bromide > Chloride > Fluoride

(iv) In S_N2 reactions the attacking nucleophile always attacks from the side in which the leaving group is attached.

(v) Methyl magnesium iodide on hydrolysis yields ethyl alcohol.

(vi) Primary, secondary and tertiary amines react with Grignard reagents in the same way.

(vii) The reactions of secondary alkyl halides may follow both S_N1 and S_N2 mechanisms.

(viii) S_N1 mechanism is a one stage process involving a simultaneous bond breakage and bond formation.

(ix) In β-elimination reactions, the two atoms or groups attached to two adjacent carbon atoms are lost under the influence of an electrophile.

(x) The reactivity order of alkyl halides is determined by the strength of carbon-halogen bond.

Answer Key.

(i)	True	(ii)	False	(iii)	True	(iv)	False	(v)	False
(vi)	False	(vii)	True	(viii)	False	(ix)	False	(x)	True

Q3. Multiple Choice Questions. Encircle the correct answer.

(i) In primary alkyl halides, the halogen atom is attached to a carbon which is further attached to how many carbon atoms:
(a) Two (b) Three (c) One (d) four

(ii) The reactivity order of alkyl halides for a particular alkyl group is:
(a) Fluoride > Chloride > Bromide > Iodide
(b) Chloride > Bromide > Fluoride > Iodide
(c) Iodide > Bromide > Chloride > Fluoride
(d) Bromide > Iodide > Chloride > Fluoride

(iii) When CO_2 is made to react with ethyl magnesium iodide, followed by acid hydrolysis, the product formed is:
(a) Propane (b) Propanoic acid (c) Propanal (d) Propanol

(iv) Grignard reagent is reactive due to:
(a) the presence of halogen atom (b) the presence of Mg atom
(c) the polarity of C—Mg bond (d) none of above

(v) S_N2 reactions can be best carried out with:
(a) Primary alkyl halides (b) Secondary alkyl halides
(c) Tertiary alkyl halides (d) All the three

(vi) Elimination bimolecular reactions involve:
(a) first order kinetics (b) second order kinetics
(c) third order kinetics (d) zero order kinetics

(vii) For which mechanisms, the first step involved is the same:
(a) E1 and E2 (b) E2 and S_N2
(c) S_N1 and E2 (d) E1 and S_N1

(viii) Alkyl halides are considered to be very reactive compounds towards nucleophiles, because:
(a) they have an electrophilic carbon
(b) they have an electrophilic carbon and a good leaving group.
(c) they have an electrophilic carbon and a bad leaving group.
(d) they have a neucleophilic carbon and good leaving group.

(ix) The rate of E1 reaction depends upon:
(a) the concentration of substrate
(b) the concentration of nucleophile
(c) the concentration of substrate as well as nucleophile
(d) None of the above

(x) Which one of the following is not a nucleophile:
(a) H_2O (b) H_2S (c) BF_3 (d) NH_3

Solved Exercise MCQs

Q.No.	Answer	Reason
(i).	(c) One	H_3C-CH_2-Cl
(ii).	(c) Iodide > Bromide > Chloride > Flouride	Reactivity $\propto \frac{1}{\text{Bond Energy}}$ as C – F has highest bond energy while C – I has lowest bond energy among them. So, this reactivity order is correct.
(iii).	(b) Propanoic acid	$CH_3-CH_2-Mg-Br + O=C=O \xrightarrow{Ether} O=C-OMgBr \xrightarrow{H_2O} O=C-OH + Mg(Br)(OH)$ (Ethyl magnesium bromide; Carbon dioxide; CH, CH, CH)
(iv).	(c) Due to Polarity of C – Mg bond	$^{\delta-}C-Mg^{\delta+}$ bond is very polar due to high electronegativity difference (1.3)
(v).	(a) Primary alkylhalide	Because stearic hindrance in Primary alkylhalide is less and primary carbocation is unstable.
(vi).	(b) Second order kinetics	Rate $= k[\text{Alkylhalide}]^1[\text{base}]^1$ $n = 1+1 = 2^{nd}$ order
(vii).	(d) E_1 and S_N1	In both mechanisms, first step is ionization of tertiary alkyl halide.
(viii).	(b) They have electrophilic carbon and good leaving group	$Nu^- + -C-L \longrightarrow Nu-C- + L^-$

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(ix).	(a) Concentration of substrate	First step is rate determing step in which reactant is substrate.
(x).	(c) BF_3	BF_3 has no electron pair or negative charge on central atom 'B'. So it attracts electrons and acts as electrophile.

Previous Board Questions

1. Write down the names of the following compounds according to IUPAC system:
   (a) CH_2Cl_2 **(b)** $(CH_3-CH_2)_3CBr$
2. Starting from ethyl Iodide prepares Propanoic Acid.
3. Write down the four possible isomers of $C_5H_{11}Cl$ and name according to IUPAC system.
4. Give the four points of difference between S_N1 and S_N2 reactions.
5. Give the mechanism for addition of Grignard's reagent to CO_2. Giving carboxylic acids.
6. Convert ethyl Alcohol into their respective halides by using PCl_3 and PCl_5.
7. How will you get 2-butanol from ethyl magnesium bromide?
8. How does Ethyl bromide react with
   (i) Aqueous KOH **(ii)** Alcoholic KOH
9. What do you understood by the term β-elimination reaction?
10. What products are formed when the following compounds are treated with Ethylmagnesium bromide.
    (a) HCHO (b) $(CH_3)_2CO$
11. Write two methods for the preparation of alkyl halides.
12. How do you differentiate between E1 and E2 mechanism.
13. Grignard reagent is an important organic reagent. Justify the statement.
14. Show the mechanism for the reaction of acetone with Grignard's reagent.
15. How methyl chloride and ethyl chloride will react with sodium-lead alloy?
16. What are primary, secondary and tertiary alkyl halides? Give examples of each.
17. How the nature of alkyl group changes when alkyl halide is converted to Grignard reagent?
18. Give mechanism of SN_1 reaction.
19. Write reaction of the Grignard Reagent with alcohol and carbon dioxide.
20. How Grignard reagent is used to prepare Tertiary alcohol?
21. Write down equations for the reactions of Grignard reagent with HCN and CH_3CHO.

For Answers Study
Scholar's CHEMISTRY (Objective) Part II
Available in Market By the same Authors
- Entry Tesy MCQ's
- Additional MCQ's
- Past Board MCQ's
- Short Questions with Answers
- Previous Board papers

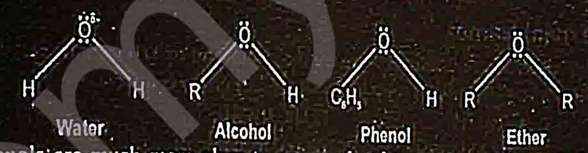
And Many More in the Objective Chemistry

CHAPTER 11

ALCOHOLS, PHENOLES AND ETHERS

Introduction

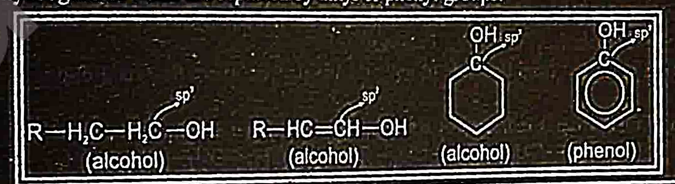
Alcohols, phenols and ethers are classes of organic compounds which are much closer to water in structure and hence considered as derivatives of water.



- Alcohols and phenols are much more close to one another in structure and properties. Both contain hydroxyl (-OH) group so they may also be termed as

(i) Hydroxy derivatives of alkanes are called alcohols.
(ii) Hydroxy derivatives of benzene are called phenols.

- In ether both hydrogens of water are replaced by alkyl or phenyl groups.



ALCOHOLS

Organic compounds containing hydroxyl (–OH) as functional group are called alcohols.

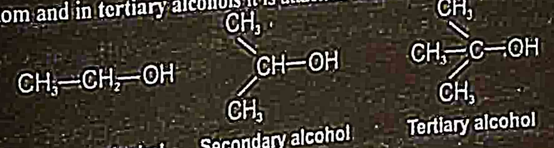
- They are represented by a general formula ROH where R is an alkyl group which may be CH_3—, CH_3CH_2 —, $(CH_3)_2CH$— and C_6H_5 —CH_2—, etc.

Classification of Alcohols

Alcohols are classified into

(i) **Monohydric Alcohols**

- They contain one hydroxyl group (–OH).
- They are further classified into primary, secondary and tertiary alcohols.
- In **primary alcohols**, –OH functional group is attached with primary carbon atom, in **secondary alcohols** with secondary carbon atom and in **tertiary alcohols** it is attached with a tertiary carbon atom.



(ii) **Dihydric Alcohols**

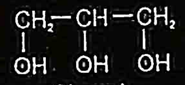
- They contain two hydroxyl groups (–OH).



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(iii) Polyhydric Alcohols

- They contain more than two hydroxyl groups (–OH).



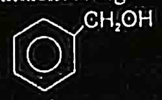
Glycerol

Nomenclature of alcohols

There are two systems of naming alcohols

(a) Common or Trivial Names

Lower and simpler alcohols are usually known by their **common or trivial names,** obtained by adding the name of alcohol after the name of the alkyl group to which the OH group is attached. e.g.

CH_3OH	C_2H_5OH	$C_6H_5CH_2OH$ or 
Methyl alcohol	Ethyl alcohol	Benzyl alcohol

(b) IUPAC Names

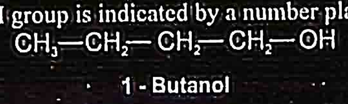
In this system, the alcohols are named according to the following rules.

(i) The longest chain of carbon atoms containing the hydroxyl group is taken as parent hydrocarbon. The ending 'e' of alkane is replaced by ol, e.g;

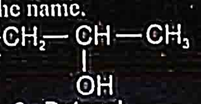
CH_3OH	C_3H_7OH	$C_5H_{11}OH$
Methanol	Propanol	Pentanol

(ii) The numbering is started from that side of longest carbon chain where the OH group is given the lowest possible number.

The position of OH group is indicated by a number placed before the name.

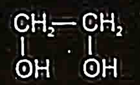


1 - Butanol

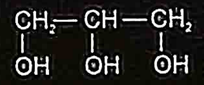


2 - Butanol

(iii) If more than one OH groups are attached, they are indicated by an appropriate suffix diol, triol, etc. e.g.

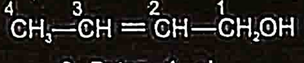


1,2-Ethanediol



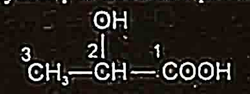
1,2,3-Propanetriol

(iv) The unsaturated alcohols are numbered in such a way that hydroxyl group rather than the point of unsaturation gets the lower number e.g.,

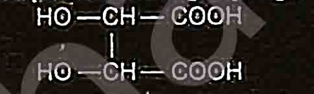


2 - Buten - 1 - ol

(v) When hydroxyl group is not a preferred functional group as in hydroxy acids, aldehydes and ketones, the substituent name hydroxy is used as a prefix to indicate the position of OH group, e.g.;

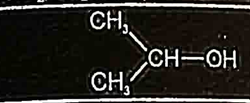
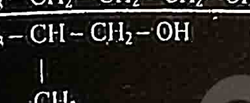
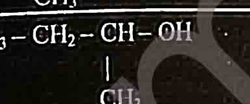
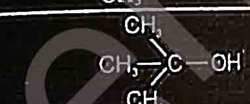


2-Hydroxy propanoic Acid
(Lactic Acid)



2,3-Dihydroxy butane-1,4-dioic Acid
(Tartaric Acid)

The names of some alcohols in the two systems are given below

FORMULA	COMMON NAME	IUPAC NAME
CH_3OH	Methyl alcohol	Methanol
CH_3CH_2OH	Ethyl alcohol	Ethanol
$CH_3CH_2CH_2OH$	Propyl alcohol	1-Propanol
	Iso-propyl alcohol	2-Propanol
$CH_3-CH_2-CH_2-CH_2-OH$	n – Butyl alcohol	1 – Butanol
	Iso-Butyl alcohol	2-Methyl-1-propanol
	sec-Butyl alcohol	2-Butanol
	ter-Butyl alcohol	2-Methyl-2-propanol

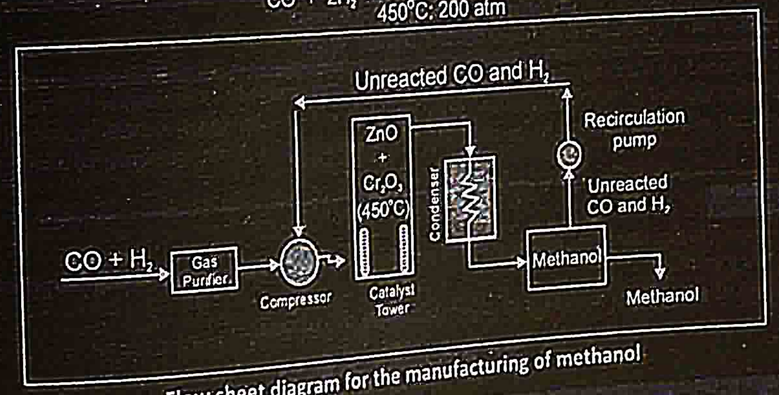
Industrial Preparation of Alcohols

Q.5 How is methyl alcohol obtained on large scale?

Methanol (CH_3OH)

- Formerly methanol was prepared by distillation of wood. That is why it is also called as **wood spirit.**
- Now-a-days methanol is prepared from carbon monoxide and hydrogen or water gas as follows:.

$$CO + 2H_2 \xrightarrow[450°C;\ 200\ atm]{(ZnO + Cr_2O_3)} CH_3OH$$



Flow sheet diagram for the manufacturing of methanol

Procedure

- First of all a mixture of carbon monoxide and hydrogen is purified.
- It is compressed under a pressure of 200 atmospheres and taken into a reaction chamber by means of coiled pipes.
- Here the catalyst is heated upto 450-500 °C.
- Gases react to form methanol vapours which are passed through a condenser to get methanol.
- Unreacted gases are recycled through compressor to reaction chamber.

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Ethanol (C_2H_5OH)

Ethanol is prepared on industrial scale world over, by the process of fermentation.

Fermentation

It is a biochemical process which occurs in the presence of certain enzymes secreted by microorganisms such as yeast.

Necessary conditions:

(i) Optimum temperature for fermentation is 25-35°C.
(ii) Proper aeration
(iii) Dilution of solution
(iv) Absence of any preservative

- Required temperature is 27°C
- Fermentation completes in three days
- It is an exothermic process.

Raw Material

In Pakistan ethanol is prepared by the fermentation of molasses, starch grains or fruit juices.

From Molasses

The residue obtained after the crystallization of sugar from concentrated sugarcane juice is called molasses. It undergoes fermentation in the presence of enzymes present in yeast to give ethanol.

$$\underset{\text{Molasses}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{Yeast}]{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[\text{Yeast}]{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

No enzyme = No fermentation

From Starch

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[\text{Yeast}]{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{Yeast}]{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[\text{Yeast}]{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

Q. Why absolute alcohol cannot be prepared by fermentation process?
Q. Only 14% alcohol can be prepared by fermentation process. Why? (LHR 09)

Alcohol obtained by fermentation is only upto 12% and never exceeds 14% because beyond this limit enzymes become inactive. This alcohol is distilled again and again to obtain 95% alcohol which is called rectified spirit. Absolute alcohol can also be obtained by re-distillation of rectified spirit in the presence of CaO which absorbs its moisture.

Denaturing of Alcohol

- Sometimes ethanol is denatured by addition of 10% methanol to avoid its use for drinking purposes. Such alcohol is called methylated spirit.
- A small quantity of pyridine or acetone may also be added for this purpose.

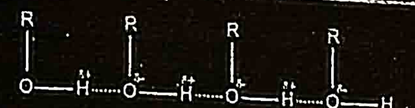
Other Methods of Preparation of Alcohols

Alcohols can be obtained by the hydration of alkenes and by the reaction of Grignard reagents with aldehydes or ketones.

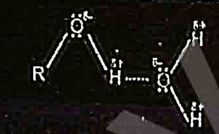
Physical Properties

(i) **Physical state:** Lower alcohols are generally colourless toxic liquids with characteristics sweet smell and burning taste.

(ii) **Solubility:** They are readily soluble in water but solubility decreases in higher alcohols. The solubility of alcohols is due to hydrogen bonding which is more prominent in lower alcohols but less prominent in higher alcohols.



Hydrogen bonding in alcohol



Hydrogen bonding between water and alcohol

Compound	Melting Point (°C)	Boiling Point (°C)
CH_3OH	-97.8	65.0
CH_3CH_2OH	-114.7	78.5
$CH_3CH_2CH_2OH$	-126.5	97.4
$CH_3(CH_2)_2OH$	-89.5	117.3
$CH_3(CH_2)_3OH$	-79.0	138

(iii) **Melting and boiling points:** Melting and boiling points of alcohols are higher than corresponding alkanes. Methyl alcohol and ethyl alcohol are liquids while methane and ethane are gases. This is also due to hydrogen bonding which is present in alcohols but absent in alkanes.

MCQ
Which among the following compounds has greater boiling point than alcohols?
a) Alkanes b) Aldehydes
c) Ethers d) Ketones

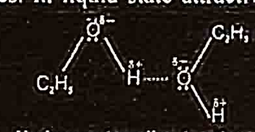
Q.11 (i) Why ethyl alcohol is a liquid while methyl chloride is a gas? (Rwp 09)

Ans. Ethyl Alcohol is Liquid but Methylchloride is a Gas

The physical state of a substance depends upon the strength of intermolecular forces. In liquid state attractive forces are stronger than in gaseous state.

Ethylalcohol – a Liquid:

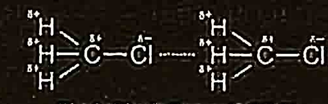
In C_2H_5OH (ethylalcohol), strong hydrogen bonding is present due to which it exists as liquid. Moreover, it has high polarizability due to which it has strong van der Waal's forces.



Hydrogen bonding in ethanol

Methylchloride – a Gas:

Less polarizability and weaker attractive forces (dipole-dipole forces) are the main reasons for gaseous state of methylchloride (CH_3Cl).



Dipole Dipole Forces in CH_3Cl

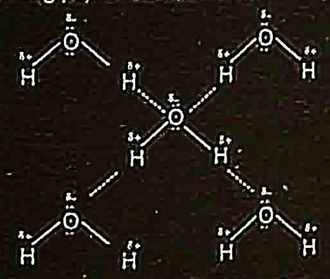
Q.11 (ii) Ethanol has higher boiling point than diethyl ether. Why?

Ans: Higher Boiling Point of Ethanol than Diethyl ether

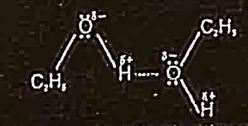
Boiling point of a compound depends upon the strength of intermolecular forces present in it. The intermolecular forces in **ethanol** are strong hydrogen bonding due to which ethanol has higher boiling point (78.5°C). On the other hand, diethyl ether has weak London dispersion forces due to which its boiling point is lower (34.6°C) than that of ethanol.

Q.11 (v) Water has highest boiling point than ethanol:

Ans. Boiling point of a liquid depends upon strength of intermolecular forces. Stronger the intermolecular forces higher is the boiling point and vice versa.



Hydrogen bonding in water



Hydrogen bonding in ethanol

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Since water can form two hydrogen bonds per molecule while ethanol can form only one hydrogen bond per molecule, therefore the extent of H-bonding in water is more than in alcohol. That's why H_2O has higher boiling point (100°C) than boiling point of ethanol (78.5°C).

Reactions of Alcohols

Alcohols react with other reagents in two ways

Reaction in which C – O bond breaks (S_N Reactions)	Reaction in which O – H bond breaks (ES Reactions)
∘ If a nucleophile attacks on an alcohol, it is the C—O bond which breaks. As a result a carbocation is formed. $CH_3-\overset{\delta+}{C}H_2-\overset{\delta-}{O}H \xrightarrow{\text{Nucleophile}} CH_3-CH_2^+ + OH^-$	∘ If an electophile attacks on an alcohol, it is the O—H bond which breaks. $CH_3-CH_2-\overset{\delta-}{O}-\overset{\delta+}{H} \xrightarrow{\text{Electrphile}} CH_3-CH_2-\bar{O}+H^+$
Order of reactivity Tertiary alcohol > Secondary alcohol > Primary alcohol	**Order of reactivity** CH_3OH > Primary alcohol > Secondary alcohol > Tertiary alcohol
Reactions 1. $C_2H_5OH + SOCl_2 \xrightarrow{\text{Pyridine}} C_2H_5Cl + SO_2 + HCl$ (Ethanol, Thionyl chloride, Ethyl chloride) 2. $C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$ 3. $C_2H_5OH + HNH_2 \xrightarrow{ThO_2} C_2H_5NH_2 + H_2O$ (Ethyl amine)	**Reactions** 1. $2C_2H_5OH + 2Na \longrightarrow 2C_2H_5\bar{O}Na^+ + H_2$ (Sodium ethoxide) 2. $C_2H_5OH + CH_3^{\delta-}Mg^{\delta+}I^{\delta-} \longrightarrow CH_4 + Mg(I)(OC_2H_5)$ 3. $C_2H_5OH + CH_3COOH \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} CH_3COOC_2H_5 + H_2O$ (Ethyl acetate)

Order of Stability of Carbocations is

$H_3C-\overset{\oplus}{C}(CH_3)_2$ > $HC^{\oplus}(CH_3)_2$ > $CH_3-H_2C^{\oplus}$ > $^{\oplus}CH_3$

Ter. carbocation > Sec. carbocation > Pri. carbocation > Methyl carbocation

Order of Stability of Alkoxide ions is

$CH_3-\bar{O}$ < $CH_3-H_2C-\bar{O}$ < $HC(CH_3)_2-\bar{O}$ < $H_3C-C(CH_3)_2-\bar{O}$

Methoxide ion < Pri. Alkoxide ion < Sec. Alkoxide Ion < Ter. Alkoxide Ion

Some Other Reactions of Alcohols

(i) Oxidation

Oxidation of alcohols convert them into aldehydes and ketones. The best reagent for this purpose is acid dichromate.

∘ Primary alcohols oxidize to aldehydes.

$$CH_3-CH_2OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-CHO + H_2O$$

Ethanal (acetaldehyde)

∘ Secondary alcohols oxidize to ketones.

$$CH_3-CH(OH)-CH_3 + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-CO-CH_3 + H_2O$$

2-Propanol → Propanone (acetone)

∘ Tertiary alcohols are resistant to oxidation. In the presence of acid dichromate they undergo elimination reaction to give alkenes.

$$(CH_3)_3C-OH \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_2=C(CH_3)-CH_3 + H_2O$$

2-methyl-2-Propanol → 2-Methylpropene

Q.11 (iv) Ethanol gives different products with conc. H_2SO_4 under different conditions.

(ii) Dehydration

Alcohols react with con. H_2SO_4 and give different products at different temperatures.

$$C_2H_5OH \xrightarrow[180°C]{\text{Conc. } H_2SO_4} CH_2=CH_2 + H_2O$$

Ethanol → Ethene — Breakage of C – O & C – H bond

$$2C_2H_5OH \xrightarrow[140°C]{\text{Conc. } H_2SO_4} C_2H_5OC_2H_5 + H_2O$$

Ethanol → Diethyl ether — Breakage of C – O & O – H bond

(iii) Reactions with Phosphorus Halides (PCl_3, PCl_5)

$$3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + H_3PO_3$$

$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl$$

Q.4 How will you distinguish between primary, secondary and tertiary alcohols?

Ans. Lucas Test

Primary, secondary and tertiary alcohols are identified and distinguished by reacting them with conc. HCl in anhydrous $ZnCl_2$. This is called as Lucas test. In Lucas test alcohols convert into corresponding alkyl halides.

Lucas Reagent
A mixture of conc. HCl and anhydrous $ZnCl_2$ is called Lucas Reagent.

(i) Primary Alcohols:

Primary alcohol forms an oily layer with $ZnCl_2$/HCl on heating.

$$R-CH_2-OH + HCl \xrightarrow[\text{Heat}]{ZnCl_2} R-CH_2-Cl + H_2O$$

(Primary alcohol) → (Primary alkyl chloride)

(ii) Secondary Alcohols:

Secondary alcohols form an oily layer in five to ten minutes.

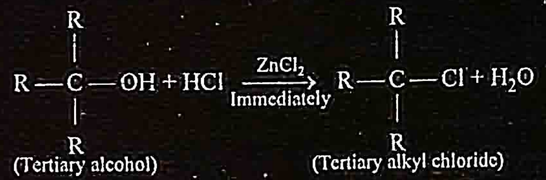
$$R-CH(R)-OH + HCl \xrightarrow[5\text{-}10 \text{ min}]{ZnCl_2} R-CH(R)-Cl + H_2O$$

(Secondary alcohol) → (Secondary alkyl chloride)

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(iii) Tertiary alcohols:

Tertiary alcohols form oily layer immediately.



Q10. How will you distinguish between: (iii) Methanol and ethanol

Ans: (iii) Methanol and Ethanol:

Methanol and ethanol can be distinguished by **iodoform test.**

Methanol	Ethanol
◦ Methanol does not give iodoform test $CH_3–OH+I_2+NaOH \longrightarrow$ No yellow ppt	◦ Ethanol gives iodoform test In iodoform test, ethanol reacts with iodine in the presence of NaOH and gives yellow coloured crystals of iodoform. $CH_3–CH_2–OH+4I_2+6NaOH \longrightarrow CHI_3+HCOONa+5NaI+5H_2O$

◦ **Those alcohols which have at least one methyl group ($-CH_3$) attached to α carbon give positive iodoform test.**
◦ **Among primary alcohols, only ethanol gives positive iodoform.**

Uses of Alcohols

Methanol

Methanol is used
- as a solvent for fats, oils, paints and varnishes.
- as antifreeze in the radiators of automobiles
- for denaturing of alcohol.

Haloform	Formula	Appearance
Fluoroform	CHF_3	Colourless gas
Chloroform	$CHCl_3$	Colourless liquid
Bromoform	$CHBr_3$	Colourless liquid
Iodoform	CHI_3	Bright yellow crystals

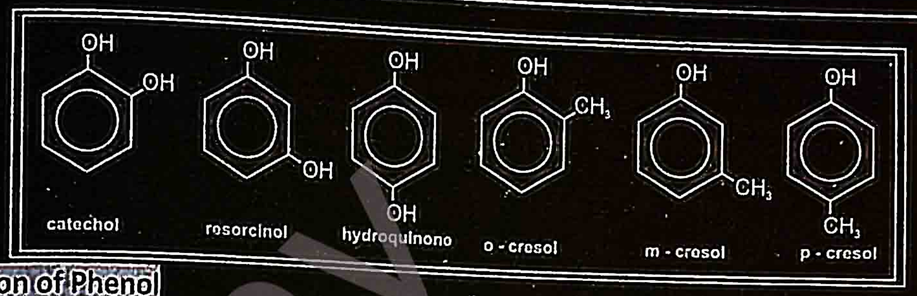
Ethanol

Ethanol is used
- as a solvent, as a drink and as a fuel in some countries.
- in pharmaceutical preparations.
- as a preservative for biological specimen.

PHENOL

"Aromatic compounds which contain one or more –OH groups directly attached with carbon of benzene ring are called Phenols".

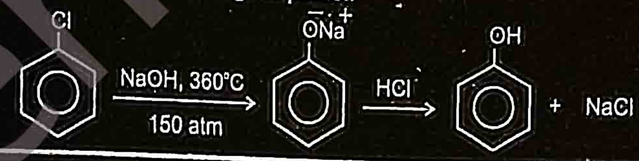
- The simplest example is phenol which is also known as Carbolic acid i.e. C_6H_5OH.
- It was first obtained from coal tar by Runge in 1834.



Preparation of Phenol

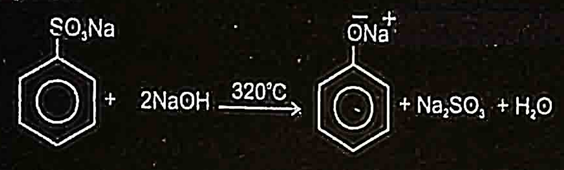
1. From Chlorobenzene (Dow's Method)

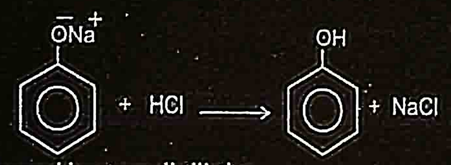
In this method chlorobenzene is treated with 10% NaOH at 360°C and 150 atmospheres pressure. Sodium phenoxide is produced which on treating with HCl gives phenol.



2. From sodium salt of benzene sulphonic acid

Sodium salt of benzene sulphonic acid reacts with NaOH at 320°C to give sodium phenoxide which on treatment with HCl gives phenol.



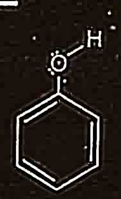


The phenol is recovered by steam distillation.

Physical Properties

- Phenol is a colourless, crystalline, deliquescent solid.
- It has characteristic phenolic odour.
- It's melting point is 41°C and boiling point is 182°C.
- It is sparingly soluble in water forming pink solution at room temperature but completely soluble above 68.5°C.
- It is poisonous and used as a **disinfectant in hospitals and washrooms.**

Acidic Behaviour of Phenol

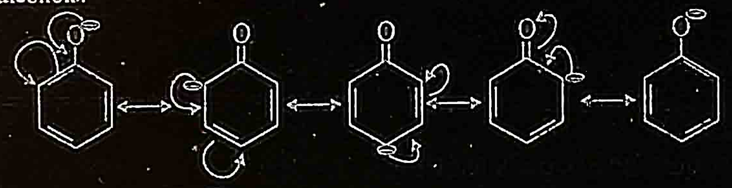


Phenol – As an Acid

- Phenol is much more acidic than water and alcohols but less acidic than carboxylic acids.
  Relative acidic strength of alcohol, phenol, water and carboxylic acid is as follows.
  Carboxylic acid > phenol > water > alcohol
- It dissolves readily in alkalies but it is too weak to affect the litmus paper or to evolve CO_2 from carbonates.
- Its dissociation constant (K_a) is 1.3×10^{-10}.
- Phenol is partially soluble in water and its solution has a pH of around 5 or 6.

Reason of acidic behaviour

The reason why phenol is acidic lies in the nature of the phenoxide ion. The negative charge on oxygen atom can become involved with the π- electron cloud on the benzene ring. The negative charge is thus delocalized in the ring and the phenoxide ion becomes relatively stable. This type of delocalization is not possible with alcohols. This makes phenol different from aliphatic alcohols.



Acidic strength ∝1/pKa

Acids	pKa
Sulphuric acid	-10.0
Hydrochloric acid	-9.0
Acetic acid	4.75
Phenol	10.0
Water	15.7
Ethanol	15.9

Reactions of Phenol

Phenol shows two types of reactions.

(a) Reactions due to – OH group

(b) Reactions due to benzene ring

Reactivity towards nucleophile

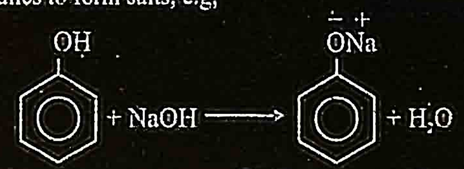
Phenols are less reactive to nucleophiles so nucleophilic attack is less favoured, i.e. – OH is not easy to replace.

While electrophilic attack on the ring is easy.

(a) Reactions of Phenol Due to -OH Group

(i) Salt Formation

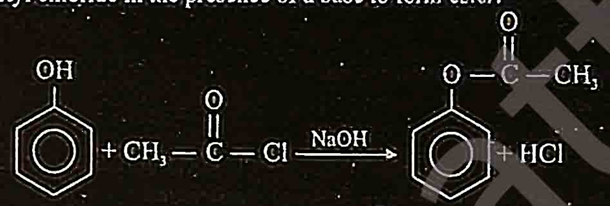
Phenol reacts with alkalies to form salts, e.g;



Sodium phenoxide

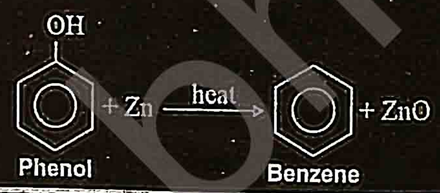
(ii) Ester Formation

Phenol reacts with acetyl chloride in the presence of a base to form ester.



Phenyl acetate

(iii) Reduction with Zn

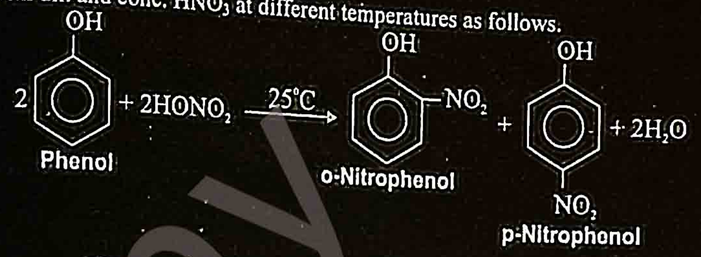


Phenol Benzene

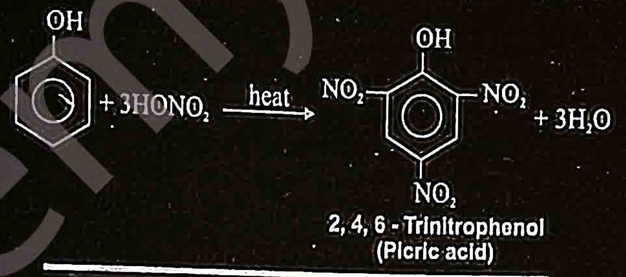
(b) Reactions of Phenol Due to Benzene Ring

(i) Nitration

Phenol reacts with dil. and conc. HNO_3 at different temperatures as follows.



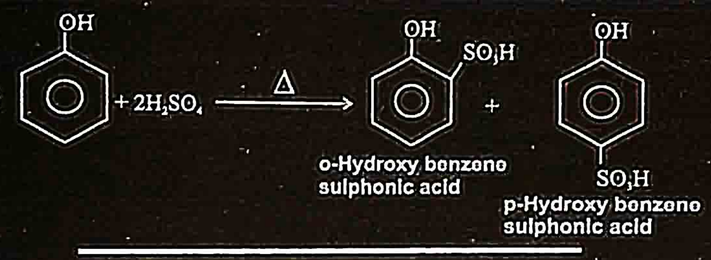
Phenol o-Nitrophenol p-Nitrophenol



2, 4, 6 - Trinitrophenol (Picric acid)

(ii) Sulphonation

Phenol reacts with conc. H_2SO_4 at room temperature giving ortho and para hydroxy benezene sulphonic acids.



o-Hydroxy benzene sulphonic acid p-Hydroxy benzene sulphonic acid

(iii) Halogenation

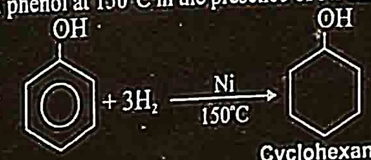
An aqueous solution of phenol reacts with bromine water to give white ppt. of 2, 4, 6-Tribromophenol.



2, 4, 6 - Tribromophenol

(iv) Hydrogenation

When hydrogen is passed through phenol at 150°C in the presence of Ni catalyst, it gives cyclohexanol.

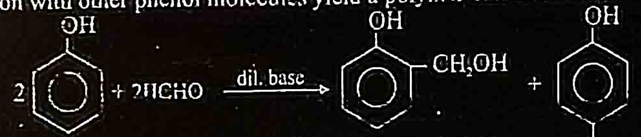


Cyclohexanol

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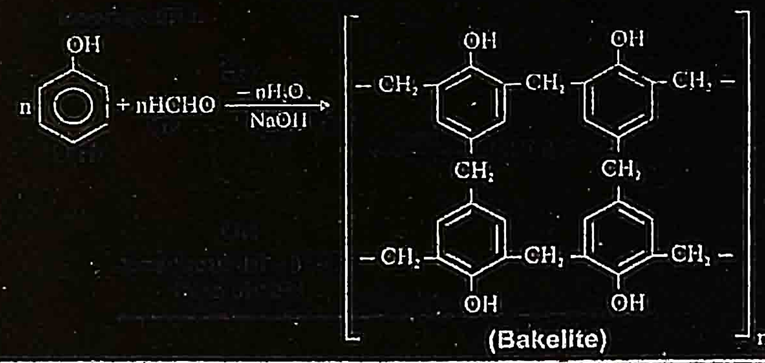
(v) Reaction with Formaldehyde

Phenol reacts with formaldehyde (methanal) in the presence of acid or alkali to give hydroxy benzyl alcohol which on further reaction with other phenol molecules yield a polymer called bakelite.



o - Hydroxybenzyl alcohol

p - Hydroxybenzyl alcohol



(Bakelite)

ETHERS

Ethers are classified into two categories:

(i) **Simple or symmetrical ethers,** (R – O – R) which contain two same alkyl or aryl or phenyl groups e.g. dimethyl ether (CH_3OCH_3) and diethyl ether ($CH_3 – CH_2 – O – CH_2 – CH_3$).

(ii) **Mixed or unsymmetrical ethers,** (R – O – R') which contain different alkyl or aryl or phenyl groups, e.g., ethyl methyl ether ($CH_3 – O - CH_2 – CH_3$) etc.

Nomenclature

IUPAC Names

In IUPAC system the large alkyl (R) group is taken as parent molecule and given the last name (suffix) while the smaller alkyl group along with oxygen is used as prefix and given the name alkoxy (e.g. methoxy, ethoxy, propoxy, etc). IUPAC names are not common as they are difficult.

Common Names

Usually ethers are known by their common names, as given below;

Formula	Common Names	IUPAC
CH_3OCH_3	Dimethyl ether	Methoxy methane
$CH_3OC_2H_5$	Methyl ethylether	Methoxy ethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxy ethane
$C_2H_5O\,CH_2 – CH_2 – CH_3$	Ethyl n-propylether	Ethoxy n – propane
$CH_3OC_6H_5$	Methyl phenyl ether (Anisol)	Methoxy benzene

Preparation of Ethers

Ethers are prepared from alcohols either directly or indirectly. Usually they are obtained by the following methods.

(i) By Williamsons synthesis

Alcohols are reacted with metallic sodium to form alkoxides. This alkoxide ion is a strong nucleophile and readily reacts with alkyl halide to produce an ether.

$$2C_2H_5OH + 2Na \longrightarrow 2C_2H_5O^-Na^+ + H_2$$

$$C_2H_5O^-Na^+ + C_2H_5Br \longrightarrow C_2H_5OC_2H_5 + NaBr$$

(ii) Alkyl halides are heated with dry silver oxide to form ethers

$$2C_2H_5Br + Ag_2O \longrightarrow C_2H_5OC_2H_5 + 2AgBr$$

MCQ's

The product formed when an alkyl halide is treated with moist Ag_2O

(a) Alcohol
(b) Carboxylic acid
(c) Ether
(d) Alkane

Physical Properties

- Usually ethers are volatile liquids, highly inflammable with low boiling points.
- They are slightly soluble in water but freely soluble in organic solvents.
- Ether molecules do not show hydrogen bonding with one another but they show weak hydrogen bonding with water molecules due to which they are slightly soluble in water.

Chemical Reactivity

Ethers are comparatively inert substances. The reagents like ammonia, alkalies, dilute acids and metallic sodium, have no action on ethers in cold state. Moreover, they are not oxidized or reduced easily. However, ethers show some reactions, e.g.

(i) With hydrogen iodide ethers give alcohols which can react further to give alkyl iodides.

$$C_2H_5OC_2H_5 + HI \longrightarrow C_2H_5 – \overset{H}{O^+} – C_2H_5 + I^-$$

(Oxonium ion)

$$C_2H_5 – \overset{H}{O^+} – C_2H_5 + I^- \longrightarrow C_2H_5OH + C_2H_5I$$

(ii) Ethers also react with hot phosphorus pentachloride to give alkyl chloride.

$$C_2H_5 – O – C_2H_5 + PCl_5 \longrightarrow 2C_2H_5Cl + POCl_3$$

KEY POINTS

1. Alcohols and Phenols are hydroxyl derivatives of aliphatic and aromatic hydrocarbons.
2. General formula for a alcohol is ROH, for Phenol Ph OH, and for ether it is ROR.
3. Alcohols are usually named by replacing 'e' for the alkane with 'ol'.
4. In Pakistan ethanols is prepared commercially from molasses.
5. Fermentation is a biochemical phenomenon which may occur naturally or artificially.
6. Ethyl alcohol obtained by fermentation is less than 12% concentrated.
7. Ethyl alcohol gives different products when reacts with H_2SO_4 of different concentrations.
8. Ethyl alcohol is used as a solvent, as a beverage and as a fuel.
9. Primary, secondary and tertiary alcohols can be distinguished by Lucas test.
10. Picric acid is a phenol which behaves like an acid.

SOLVED OBJECTIVE EXERCISE

Q1. **Fill in the blanks.**

(i) Primary, secondary and tertiary alcohols can be identified by ____ test.
(ii) Oxidation of ____ alcohols give ketones.
(iii) Alcohols on heating with ____ give alkenes at high temperature.
(iv) Alcohols have ____ boiling points than ethers due to stronger hydrogen bonding.
(v) Williamsons synthesis is used to prepare ____.
(vi) _____ is also called wood spirit.
(vii) Carbolic acid is the other name of ____.

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(viii) Primary, secondary and tertiary alcohols can be prepared by reacting Grignard reagent with ____.
(ix) Alcohols and ____ react to produce esters.
(x) ____ is used as anti- freezing agent in automobile radiator.
(xi) The process of conversion of starch into alcohol with the help of micro – organisms is called ____.
(xii) Ketones on reduction give ____ alcohols.

Answer Key.

(i)	Lucas	(ii)	Secondary
(iii)	Conc.H_2SO_4	(iv)	Higher
(v)	Ethers	(vi)	Methyl alcohol
(vii)	Phenol	(viii)	Carbonyl compounds
(ix)	Carboxylic acids	(x)	Methyl alcohol
(xi)	Fermentation	(xii)	Secondary.

Q2. Indicate True or false.

(i) Methylated spirit contains 95% methyl alcohol and 5% ethyl alcohol.
(ii) Ethyl alcohol is a very good anti-freezing agent.
(iii) Methanol is also called wood spirit.
(iv) Only 14% ethyl alcohol can be prepared by fermentation.
(v) Ethers do not show hydrogen bonding.
(vi) Alcohols are more acidic then phenols.
(vii) Phenol is more soluble in water than lower alcohols.
(viii) Alcohols are more basic than ethers.
(ix) Ethers have higher boiling point than alcohols and phenols.
(x) Methanol and ethanol can be distinguished by iodoform test.

Answer Key.

(i)	False	(ii)	False	(iii)	True	(iv)	True	(v)	True
(vi)	False	(vii)	False	(viii)	False	(ix)	False	(x)	True

Q3. Multiple Choice Questions. Encircle the correct answer.

(i) Which compound shows hydrogen bonding.
(a) C_2H_6 (b) C_2H_5Cl (c) CH_3-O-CH_3 (d) C_2H_5OH

(ii) Which compound show maximum hydrogen bonding with water?
(a) CH_3OH (b) C_2H_5OH (c) CH_3-O-CH_3 (d) C_6H_5OH

(iii) Which compound is more soluble in water.
(a) C_2H_5OH (b) C_6H_5OH (c) CH_3COCH_3 (d) n- Hexanol

(iv) Which compound will have the maximum repulsion with H_2O?
(a) C_6H_6 (b) C_2H_5OH (c) $CH_3CH_2CH_2OH$ (d) $CH_3 — O — CH_3$

(v) Ethanol can be converted into ethanoic acid by
(a) Hydrogenation (b) Hydration (c) Oxidation (d) Fermentation

(vi) Which enzyme is not involved in fermentation of starch?
(a) Diastase (b) Zymase (c) Urease (d) Invertase

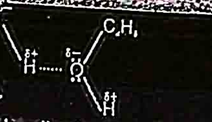
(vii) Which compound is called a universal solvent?
(a) H_2O (b) CH_3OH (c) C_2H_5OH (d) $CH_3—O—CH_3$

(viii) Methyl alcohol is not used.
(a) as a solvent (b) as an anti- freezing agent
(c) as a substitute for petrol (d) for denaturing of ethyl alcohol

(ix) Rectified spirit contains alcohol about
(a) 80% (b) 85% (c) 90% (d) 95%

(x) According to Lewis concept ethers behave as.
(a) Acid (b) Base (c) Acid as well as base (d) None of them

Solved Exercise MCQs

Q.No.	Answer	Reason
(i).	(d) C_2H_5OH	 Hydrogen bonding in ethanol
(ii).	(a) CH_3OH	As the length of carbon chain increases the hydrogen bounding of alcohol with water decreases.
(iii).	(a) C_2H_5OH	Due to hydrogen bonding with H_2O it is soluble in water.
(iv).	(a) C_6H_6	Image Structure Benzene is non-polar while H_2O is polar so C_6H_6 (benzene) is insoluble in water.
(v).	(c) Oxidation	$C_2H_5OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3CHO \xrightarrow{[O]} CH_3COOH$ (Ethanol) (Ethanoic acid)
(vi).	(c) Urease	$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{Diastase}} nC_{12}H_{22}O_{11}$ $C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Maltase}} 2C_6H_{12}O_6$ $C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$
(vii).	(a) H_2O	Water dissolves almost all compounds except some organic compounds so it is a universal solvent.
(viii).	(c) As a substitute for petrol	It is used as solvent, as an antifreezing agent and also for denaturating of ethylalcohol.
(ix).	(d) 95%	Rectified spirit is an azeotropic mixture.
(x).	(b) Base	Ether can give lone pair of electrons so they are Lewis base.

SOLVED EXERCISE

Q10. How will you distinguish between:
(i) An alcohol and a phenol (ii) An alcohol and an ether
(iii) Methanol and ethanol (iv) A tertiary alcohol and a primary alcohol
(v) 1-Propanol and 2-Propanol

Ans. (i) An alcohol and a phenol

Alcohol	Phenol
It gives positive iodoform test i.e. on treating with conc. HCl in the presence of anhydrous $ZnCl_2$, an alcohols forms oily layer. $R-CH_2-OH + HCl \xrightarrow[heat]{ZnCl_2} R-CH_2-Cl + H_2O$	Phenol does not give oily layer when react with HCl in the presence of anhydrous $ZnCl_2$. It means it does not give iodoform test. $C_6H_5OH + HCl \xrightarrow[heat]{ZnCl_2}$ No reaction

Ans (ii) An alcohol and an ether

Alcohol	Ether
It gives positive iodoform test i.e. on treating with	Ether does not form oily layer with conc. HCl and

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conc. HCl in the presence of anhydrous $ZnCl_2$, an alcohols forms oily layer. $R-CH_2-OH+HCl \xrightarrow[heat]{ZnCl_2} R-CH_2-Cl+H_2O$	anhydrous $ZnCl_2$. It means it does not give iodoform test. $R-O-R+HCl \xrightarrow{ZnCl_2}$ No Reaction

Ans. (iii) Methanol and Ethanol

Methanol	Ethanol
Methanol does not give iodoform test $CH_3-OH+I_2+NaOH \longrightarrow$ No yellow ppt	Ethanol gives iodoform test. In iodoform test, ethanol reacts with iodine in the presence of NaOH and gives yellow coloured crystals of iodoform. $CH_3-CH_2-OH+4I_2+6NaOH \longrightarrow CHI_3+HCOONa+5NaI+5H_2O$

Ans (iv) A tertiary and a primary alcohol

Tertiary alcohol	Primary alcohol
Tertiary alcohols when react with conc. HCl in the presence of anhydrous $ZnCl_2$, it gives oily layer immediately $(R)_3COH+HCl \xrightarrow[Immediatly]{ZnCl_2} (R)_3CCl+H_2O$	Primary alcohol when reacts with conc. HCl in the presence of anhydrous $ZnCl_2$, it gives oily layer on heating $R-CH_2-OH+HCl \xrightarrow[heat]{ZnCl_2} R-CH_2-Cl+H_2O$

Ans (v) 1-Propanol and 2-Propanol

1-Propanol (Primary Alcohol)	2-Propanol (Secondary Alcohol)
1-Propanol gives oily layer when it reacts with Conc. HCl in the presence of anhydrous $ZnCl_2$ only on heating. $CH_3CH_2CH_2OH+HCl \xrightarrow[heat]{ZnCl_2} CH_3CH_2CH_2Cl+H_2O$	2-Propanol gives oily layer within 5-10 minutes. When it reacts with Conc. HCl in the presence of anhydrous $ZnCl_2$. $CH_3-\underset{\displaystyle CH_3}{\overset{|}{CH}}-OH+HCl \xrightarrow[5\text{-}10\ min]{ZnCl_2} CH_3-\underset{\displaystyle CH_3}{\overset{|}{CH}}-Cl+H_2O$

Q12. How will you convert?
(i) Methanol into ethanol (ii) Ethanol into methanol
(iii) Ethanol into isopropyl alcohol (iv) Formaldehyde into ethyl alcohol
(v) Acetone into ethyl alcohol

Ans. (i) Methanol into ethanol

We can convert methanol into ethanol by following steps.

Step 1: Methanol reacts with thionyl chloride in the presence of pyridine to give methyl chloride.

$$CH_3OH + SOCl_2 \xrightarrow{Pyridine} CH_3Cl + HCl + SO_2$$

Step 2: Methyl chloride reacts with sodium in the presence of ether.

$$CH_3Cl + 2Na + CH_3Cl \xrightarrow{Ether} CH_3-CH_3 + 2NaCl$$

Step 3: Ethene reacts with Cl_2 In the presence of sunlight to give ethyl chloride.

$$CH_3-CH_3 + Cl_2 \xrightarrow{h\upsilon} CH_3-CH_2-Cl + HCl$$

Step 4: Ethyl chloride reacts with aqueous KOH to give ethanol.

$$CH_3-CH_2+Cl+KOH_{(aq)} \longrightarrow CH_3-CH_2-OH+KCl$$

Ans. (ii) Ethanol into methanol

We can convert ethanol into methanol by following steps.

Step 1: Oxidation of ethanol converts it into acetaldehyde in the presence of oxidizing agents i.e. $K_2Cr_2O_7$ & H_2SO_4.

$$CH_3-CH_2-OH+[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{O}{\overset{\|}{C}}-H+H_2O$$

Step 2: Oxidation of acetaldehyde, in the presence of oxidizing agents i.e. $K_2Cr_2O_7$, & H_2SO_4, converts it into acetic acid.

$$CH_3-\overset{O}{\overset{\|}{C}}-H+[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Step 3:

Acetic acid reacts with NaOH to form sod. Salt of acetic acid.

$$CH_3-\overset{O}{\overset{\|}{C}}-OH+NaOH \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O^-Na^+ + H_2O$$

Sodium salt of acetic acid is heated in the presence of Soda lime to form methane, releasing CO_2.

$$CH_3-\overset{O}{\overset{\|}{C}}-O^-Na^+ + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

Step 4: Halogenation of methane gives methyl chloride in the presence of sunlight.

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

Step 5: Methyl chloride reacts with aqueous KOH to give methanol.

$$CH_3Cl + KOH \xrightarrow{Aqueous} CH_3-OH+KCl$$

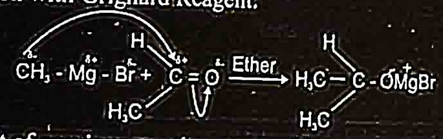
Ans (iii) Ethanol into Isopropyl alcohol:

We can convert ethanol into isopropyl alcohol by following steps.

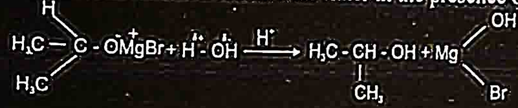
Step 1: Ethanol undergo oxidation in the presence of $K_2Cr_2O_7$ & H_2SO_4 to form acetaldehyde.

$$CH_3-CH_2-OH+[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{O}{\overset{\|}{C}}-H+H_2O$$

Step 2: Reaction with Grignard Reagent.



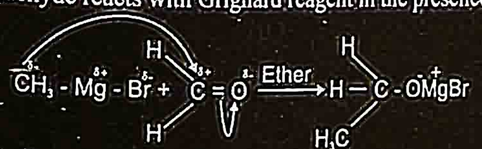
Step 3: Product of previous reaction reacts with water in the presence of H^+ and undergoes hydrolysis.



Ans (iv) Formaldehyde into ethyl alcohol.

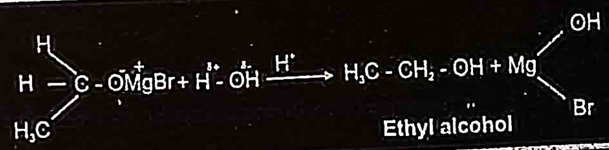
We can convert formaldehyle into ethyl alcohol by following steps.

Step 1: Formaldehyde reacts with Grignard reagent in the presence of ether to give product.



Step 2: Product of previous reaction reacts with water in the presence of H^+ to give alcohol.

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Ans. **(v) Acetone into Ethyl alcohol:**

We can convert acetone into ethyl alcohol by following steps.

Step 1: Acetone is oxidized in the presence of oxidizing agent to acetic acid.

$$CH_3 - \overset{O}{\overset{\|}{C}} - CH_3 + 3[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3 - \overset{O}{\overset{\|}{C}} - OH + H - \overset{O}{\overset{\|}{C}} - OH$$

Step 2: Carboxylic acid on reaction with lithium aluminum hydride ($LiAlH_4$) are reduced to alcohol.

$$CH_3 - \overset{O}{\overset{\|}{C}} - OH + 4[H] \xrightarrow{LiAlH_4} CH_3 - CH_2 - OH + H_2O$$

Q18. (a) Write IUPAC names of the following compounds

(i) $(CH_3)_2CH - OH$ (ii) $(CH_3)_2CH - CH_2 - OH$

(iii) $(CH_3)_3COH$ (iv) $C_2H_5 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - OH$

Ans. a) IUPAC names of following compounds.

(i) $H_3C - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3$ — 2-Propanol

(ii) $H_3C - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2 - OH$ — 2-Methyl-1-propanol

(iii) $H_3C - \underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}} - CH_3$ — 2-Methyl-2-propanol (ter – butylalcohol)

(iv) $CH_3 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{CH}}}}$ — 2-Butanol

Q.18 (b) Write structural formulas for the following compounds.

Glycol, Glycerol, Carbolic Acid, Acetophenone, Picric Acid

Ans.b) Structural formulas:

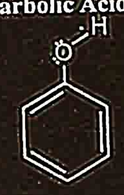
(i) Glycol:

$$\underset{\displaystyle OH}{\underset{|}{CH_2}} - \underset{\displaystyle OH}{\underset{|}{CH_2}}$$

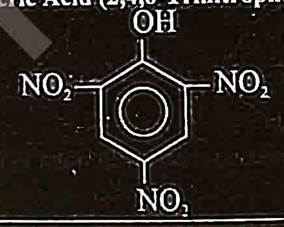
(ii) Glycerol

$$\underset{\displaystyle OH}{\underset{|}{CH_2}} - \underset{\displaystyle OH}{\underset{|}{CH}} - \underset{\displaystyle OH}{\underset{|}{CH_2}}$$

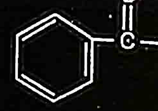
(iii) Carbolic Acid (Phenol):



(iv) Picric Acid (2,4,6-Trinitrophenol):



(v) Acetophenone (Methy phenyl ketone):



Q19. (a) Name the following compounds.

(i) $CH_3 - CH_2 - CH_2 - O - CH_3$ (ii) $C_6H_5 - OC_6H_5$

(iii) $(CH_3)_2CH - O - CH(CH_3)_2$ (iv) $CH_3 - O - C_6H_5$

(v) $CH_3 - CH_2 - CH_2 - O - CH_2 - CH_3$

Ans. Name the following.

(i) $CH_3 - CH_2 - CH_2 - O - CH_3$
Common Name: Methyl–n–propyl ether
IUPAC Name: Methoxy peopane

(ii) $C_6H_5 - O - C_6H_5$
Common Name: Diphenyl ether
IUPAC Name: Phenoxy benzene

(iii) $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - O - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_3$
Common Name: Di-iso-propyl ether
IUPAC Name: 2-Propoxy-2-Propane

(iv) $CH_3 - O - C_6H_5$
Common Name: Methyl–n–phenylether
IUPAC Name: Methoxy benzene

(v) $CH_3 - CH_2 - CH_2 - O - CH_2 - CH_3$
Common Name: Ethyl–n–propyl ether
IUPAC Name: Ethoxy propane

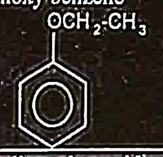
Q19. (b) Write down structural formulas of the following compounds.

Methoxy ethane, ethoxy benzene, soldum ethoxide, sodium phenoxide, propoxy propane.

Ans. Structural formulas:

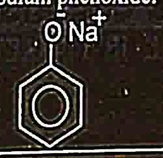
(i) Methoxy ethane
$CH_3 - CH_2 - O - CH_3$

(ii) Ethoxy benzene



(iii) Sodium ethoxide
$CH_3 - CH_2 - O^-Na^+$

(iv) Sodium phenoxide:



(v) Propoxy peopane
$CH_3 - CH_2 - CH_2 - O - CH_2 - CH_2 - CH_3$

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Previous Board Questions

1. Distinguish methyl alcohol from ethyl alcohol by means of single chemical test.
2. How phenol reacts with: (a) H_2SO_4 (b) NaOH
3. Why primary alcohols especially methanol is more reactive than other alcohols when an electrophile attacks on it?
4. What do you mean by the term denaturing of alcohols?
5. Why phenol is acidic, but alcohol is not?
6. What is rectified spirit and absolute alcohol?
7. Write equations for preparation of Ethanol from molasses by fermentation.
8. Ethanol has higher boiling point than diethyl ether. Why?
9. Prepare Phenol by
   (a) Dow's method (b) From sodium salt of benzene sulphonic Acid
10. The solubility of alcohols decreases with increasing molecular masses.
11. How Bakelite is prepared from phenol?
12. Prepare ethers by Williamson's synthesis.
13. Give four uses of phenol.
14. What is the difference between rectified spirit and absolute alcohol?
15. What is fermentation? Give necessary conditions for fermentation.
    Only 14% alcohol can be prepared by fermentation process, why?
    Convert benzene into phenol.
    What are symmetrical and unsymmetrical ethers? Give one example each?
19. Ethanol gives different products with conc. H_2SO_4 under different conditions.
20. How the resonance structures of phenoxide ion make phenol acidic?
21. Give the isomers of C_2H_6O and write their IUPAC names.
22. Give structural formulas of: (a) Carbolic acid (b) Picric acid
23. What is the action of phenol with following?
    (a) Zn (b) Bromine water
24. What is Lucas Test? Give its uses.
25. What is the reaction of Bromine water with phenol?
26. Justify ethyl alcohol is a liquid while methyl chloride is a gas?

For Answers Study
Scholar's CHEMISTRY (Objective) XII
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CHAPTER 12

ALDEHYDES AND KETONES

Introduction

Organic compounds containing the carbonyl functional group, $>C=O$ are called carbonyl compounds. In a carbonyl group, a carbon atom is bonded to oxygen with a double bond.

Classifications

Aldehydes

In aldehydes, the carbonyl group is bonded to at least one hydrogen atom, and so it occurs at the end of a chain.

An aldehyde can be represented by the general formula, $R-\overset{O}{\overset{\|}{C}}-H$, where R may be H or an alkyl group.

Examples

$H-\overset{O}{\overset{\|}{C}}-H$ Methanal

$CH_3-\overset{O}{\overset{\|}{C}}-H$ Ethanal

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$ Propanal

Ketones

In ketones, the carbonyl group is bonded to two carbon atoms, and so it occurs within a chain. A ketone may be represented by the general formula $R-\overset{O}{\overset{\|}{C}}-R$

Examples

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ Dimethyl ketone (Acetone)

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ Ethyl methyl ketone

Aldehydes and Ketones are functional group isomers of each others. e.g. Acetone and propionaldehyde.

The homologous series of both aldehydes and ketones have the general formula, $C_nH_{2n}O$.

Occurance

- Aldehydes and ketones are present in many naturally occurring compounds.
- The aldehyde group is present in most sugars.
- They are the principal constituents of a number of essential oils used as fragrances and flavours.
- Ketonic group is present in camphor and menthone (Mint).

Nomenclature of Aldehydes and Ketones

(a) Aldehydes

Common Names

- The common names of aldehydes are obtained from the common names of carboxylic acids containing the same number of carbon atoms.
- The ending -ic acid in the common name of the acid is replaced by the word aldehyde.

$H-\overset{O}{\overset{\|}{C}}-H$ Formaldehyde

$CH_3-\overset{O}{\overset{\|}{C}}-H$ Acetaldehyde

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$ Propionaldehyde

$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$ Butyraldehyde

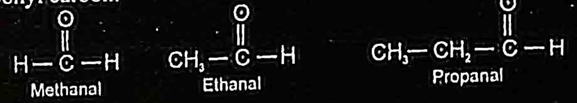
- The positions of other groups on the chain are indicated by Greek letters (α, β, γ, δ). Lettering starts on the carbon adjacent to the carbonyl group,

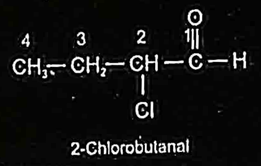
$\delta\ \gamma\ \beta\ \alpha$
$C-C-C-C-\overset{O}{\overset{\|}{C}}-H$

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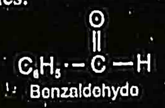
IUPAC Names

- "The IUPAC names of aldehydes are derived from the names of alkanes having the same number of carbon atoms. The letter-e in the name of the alkane is replaced with al."
- The positions of other groups on the chain are indicated by using numbers.
- Numbering starts from the carbonyl carbon.





- Aromatic aldehydes are not given IUPAC names.



(b) Ketones

Common Names

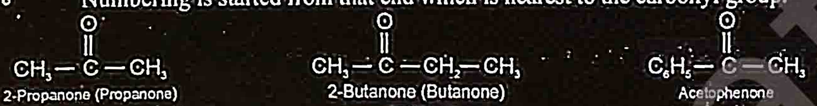
- The common names of ketones are obtained by separately writing the names of the alkyl groups attached to the carbonyl carbon.
- The word ketone is then added as a separate word. The names of the alkyl groups are written alphabetically.
- When the two alkyl groups are the same, the prefix di - is added before the name of the alkyl group.



- The positions of other groups are indicated by Greek letters, the α-carbon atom being the one adjacent to the carbonyl carbon.
- If the two alkyl groups in a ketone are the same, the ketone is said to be symmetrical, if unlike, unsymmetrical.

IUPAC Names

- The IUPAC names of ketones are derived from the names of alkanes having the same number of carbon atoms.
- The letter e in the name of alkane is replaced with the suffix -one.
- The position of the carbonyl group and of other groups on the chain are indicated by numbers.
- Numbering is started from that end which is nearest to the carbonyl group.



- Aromatic ketones are not given IUPAC names.

Formeldehyde (HCHO) is the only aldehyde which exists in gaseous state at room temperature.

Preparation of Aldehydes and Ketones

Aldehydes are obtained by the oxidation of primary alcohols whereas ketones by the oxidation of secondary alcohols. Ketones are also prepared by hydration of alkynes.

Q. Give one laboratory and one industrial method for the preparation oof formaldehyde?

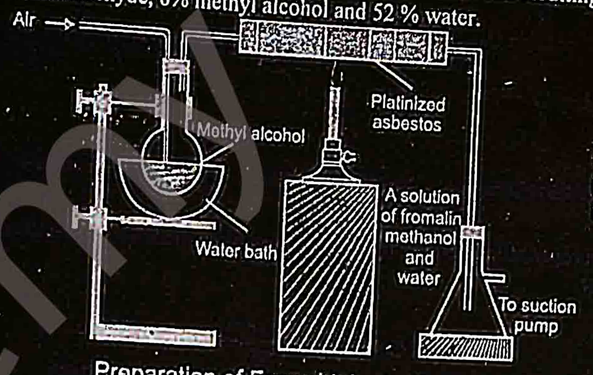
(a) Preparation of Formaldehyde (Formalin)

(i) Laboratory Method

Formaldehyde is prepared in the laboratory by passing a mixture of methyl alcohol vapours and air over platinised asbestos or copper or silver catalyst at 300°C.

$$2CH_3OH + O_2 \xrightarrow[300°C]{\text{Pt-asbestos}} 2H-\overset{O}{\overset{\|}{C}}-H + 2H_2O$$

Set up the apparatus as shown in Fig. (12.1). Air is drawn through methyl alcohol with the help of a suction pump. Methyl alcohol is oxidised to gaseous formaldehyde which is absorbed in water. The resulting mixture is called formalin. Formalin is a mixture of 40 % formaldehyde, 8% methyl alcohol and 52 % water.



Preparation of Formaldehyde (formalin)

Formalin is a trade (commercial) name of formaldehyde.

(ii) Industrial Method

Formaldehyde is manufactured by passing a mixture of methanol vapours and air over iron oxide-molybdenum oxide or silver catalyst at 500 °C.

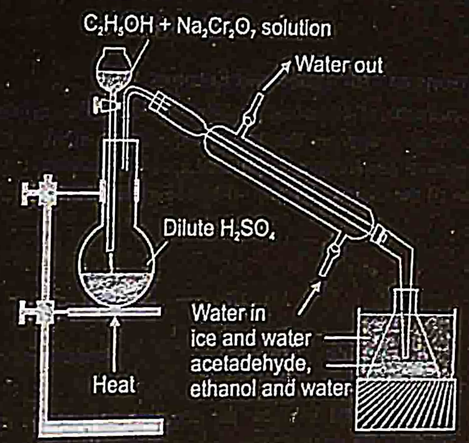
$$\underset{\text{Methanol}}{2CH_3OH} + O_2 \xrightarrow[500°C]{FeO,Mo_2O_3} 2H-\overset{O}{\overset{\|}{C}}-H + 2H_2O$$
Methanal

(b) Preparation of Acetaldehyde

(i) Laboratory method

Acetaldehyde is prepared in the laboratory by the oxidation of ethyl alcohol with acidified sodium dichromate solution.

$$CH_3CH_2OH + [O] \xrightarrow[\Delta]{Na_2Cr_2O_7 + H_2SO_4} CH_3CHO + H_2O$$



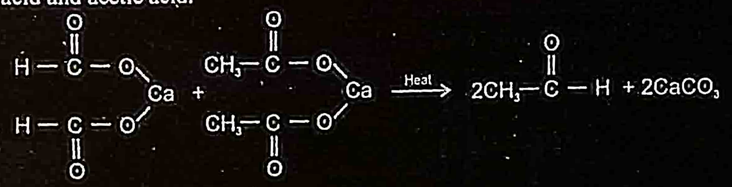
Preparation of Acetaldehyde

A mixture of ethyl alcohol and sodium dichromate solution is run into boiling dilute sulphuric acid. Immediately a vigorous reaction takes place and the acetaldehyde formed in liquid state is immediately distilled off. This prevents the

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oxidation of acetaldyde to acetic acid. Ethyl alcohol remains in solution until it is oxidised. Pure acetaldehyde is obtained by redistillation.

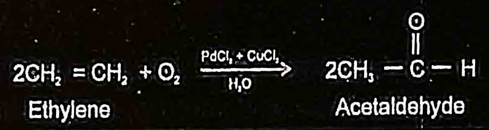
(ii) Acetaldehyde can also be prepared by the dry distillation of a mixture of calcium salts of formic acid and acetic acid.



Calcium formate Calcium acetate Acetaldehyde

(ii) Industrial Method

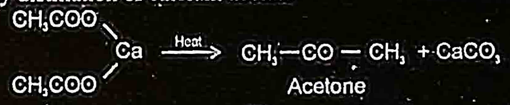
Acetaldehyde is prepared industrially by air oxidation of ethylene using palladium chloride catalyst with a cupric chloride promoter.



Ethylene Acetaldehyde

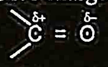
(c) Preparation of Acetone

Acetone is prepared by dry distillation of calcium acetate



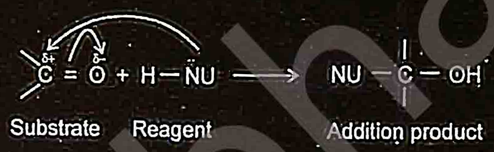
Reactivity of Carbonyl Group

The carbonyl group has a σ-bond and a π-bond. Thus it can undergo addition reactions. Most reagents react with the carbonyl group by adding to it. As oxygen is more electronegative, it tends to attract the π electrons to itself. This attraction makes the carbonyl group a polar group. The oxygen atom has a partial negative charge on it and is nucleophilic, whereas the carbon atom has a partial positive charge and is electrophilic.



Nucleophilic Addition Reactions of Aldehydes and Ketones

As a result of the unsymmetrical electronic distribution about the carbonyl group, the nucleophilic reagent can start the initial attack on the carbon. It appears that whether the initial attack is to be by a nucleophilic reagent or by an electrophilic reagent depends upon a particular reaction and upon the conditions under which that reaction is carried out. Therefore, most of the reactions of the carbonyl group will be considered to be nucleophilic addition reactions.



Substrate Reagent Addition product

In these reactions of aldehydes and ketones, the negative part of the reagent combines with the electrophilic carbon of the carbonyl group, whereas the positive part, which is usually hydrogen goes to the oxygen. The nucleophilic addition reactions of carbonyl group are catalysed by bases or acids. Remember that whether the addition is base-catalysed or acid-catalysed, the adduct is the same.

REMEMBER

- A base catalyst increases the nucleophilic character of the reagent,
- An acid catalyst promotes the nucleophilic attack by increasing the positive character (electrophilic character) of the carbonyl carbon atom.

Reactions of Carbonyl Compounds

- Nucleophilic addition reactions
- Reduction reactions
- Oxidation reactions

Nucleophilic Addition Reactions

The characteristic reactions of carbonyl compounds are nucleophilic addition reactions.

(A) BASE-CATALYSED ADDITION REACTIONS

A base-catalysed nucleophilic addition reaction will take place with a strong nucleophilic reagent. The base reacts with the reagent and generates the nucleophile. The addition is initiated by the attack of a nucleophile on the electrophilic carbon of the carbonyl group. The general mechanism of the reaction is as follows:

General mechanism

Step-I:



Step-II:



Step-III:



The base catalysed nucleophilic addition reactions of aldehydes and ketones are the following:

Q. How does formaldehyde react with the following reagents?

(i) CH_3MgI (ii) HCN (iii) $NaHSO_3$ (iv) conc. NaOH
(v) $NaBH_4/H_2O$ (vi) Tollen's reagent (vii) Fehling's reagent

1. Addition of Hydrogen Cyanide

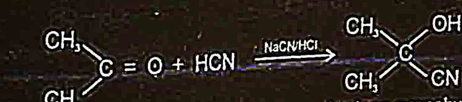
Hydrogen cyanide adds to aldehydes and ketones to form cyanohydrins. The reaction is carried out by adding slowly a mineral acid to an aqueous solution of sodium cyanide. The acid generates HCN from sodium cyanide in situ.



Formaldehyde Formaldehyde cyanohydrin



Acetaldehyde Acetaldehyde cyanohydrin

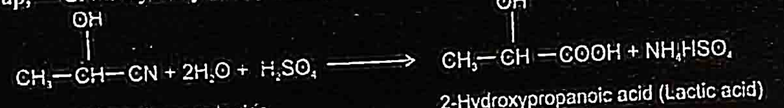


Acetone Acetone cyanohydrin

Q. How would you convert Acetaldehyde into lactic acid?

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The cyano group, — CN is hydrolysed by an aqueous acid into a carboxylic acid through an acid amide.



Use of the reaction

The reaction is used in the synthesis of α-hydroxy acids that contain one carbon atom more than number of carbon atoms in the starting aldehydes or ketones.

Mechanism

The reaction is base-catalysed because HCN has no lone pair or electrons on its carbon. The base (OH^-) generates cyanide ions which acts as nucleophiles. The mechanism of the reaction is as follows:

Step-I:



Step-II:



Step-III:



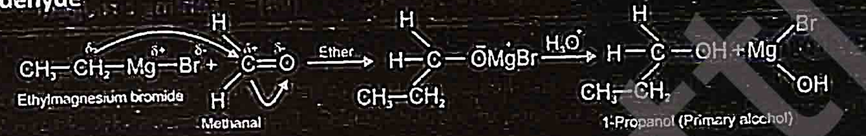
Addition product

The hydroxide ion liberated in the formation of cyanohydrin reacts with undissociated hydrogen cyanide and produces more cyanide ions, which in turn react with more carbonyl compound.

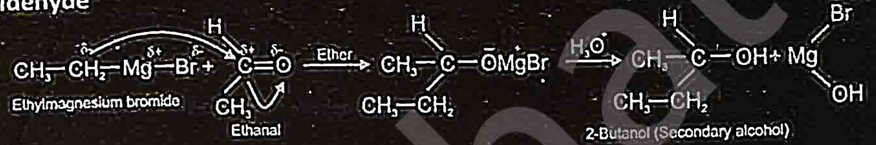
2. Addition of Grignard Reagents

Grignard reagents add to aldehydes and ketones to form adducts which on hydrolysis with a dilute mineral acid (HCl, H_2SO_4) give alcohols.

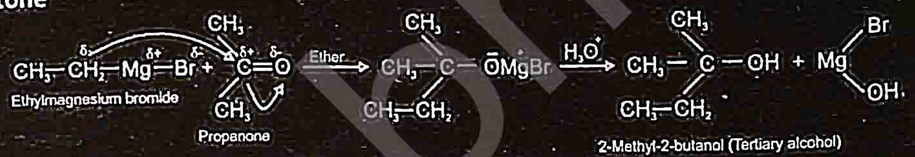
(i) With Formaldehyde



(ii) With Acetaldehyde

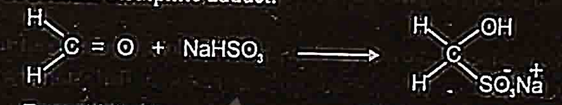


(iii) With Acetone



3. Addition of Sodium Bisulphite

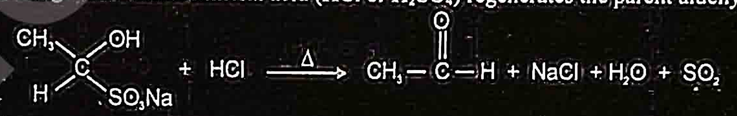
Aldehydes and small methyl ketones react with a saturated aqueous solution of sodium bisulphite to form a crystalline white precipitate of sodium bisulphite adduct.







Bisulphite on heating with a dilute mineral acid (HCl or H_2SO_4) regenerates the parent aldehyde or ketone.



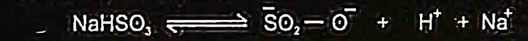
Use of the reaction

The reaction is used for the separation and purification of carbonyl compounds from non-carbonyl compounds such as alcohols.

Mechanism

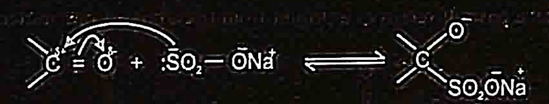
Sodium bisulphite ionizes to form sulphite ions.

Step-I:



The sulphite ion acts as a nucleophile, since the sulphur atom is more nucleophile than oxygen, a C – S bond is formed.

Step-II:



Step-III:

Proton is attached to the negatively charged oxygen atom to form bisulphite addition product.



Ketones in which both alkyl groups are larger than methyl do not react with sodium bisulphate.

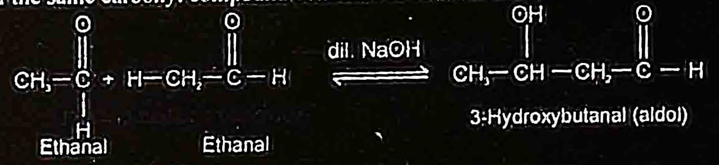
4. Condensation Reaction

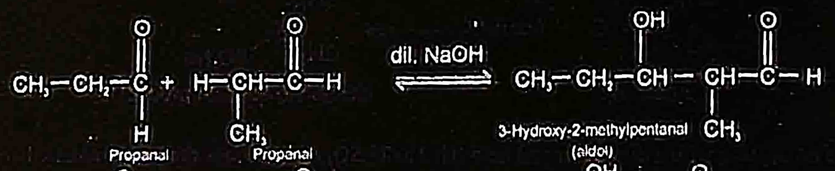
"The reactions in which two molecules of the same or different compounds combine to form a new compound with or without the elimination of a small molecule like H_2O or NH_3, are called condensation reactions."

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Aldol Condensation

- Aldehydes and ketones possessing α-hydrogen atoms react with a cold dilute solution of an alkali to form addition products known as aldols.
- The name 'aldol' is given to the product because it contains both aldehyde and alcohol functional groups.
- Note that the name aldol condensation is reserved for the reaction that starts with two identical carbonyl compounds.
- Two molecules of the same carbonyl compound condense to form an aldol.

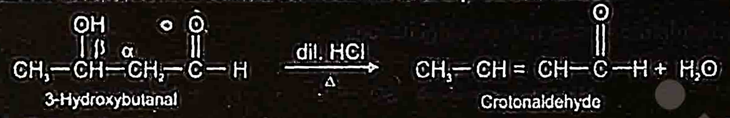






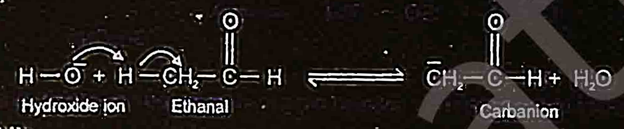
Conversion to crotonaldehyde

The aldol compound readily loses water on heating in the presence of dilute acid to form an unsaturated carbonyl compound. A carbon-carbon double bond is formed between the α-and β-carbon atoms.



Mechanism of Aldol Condensation

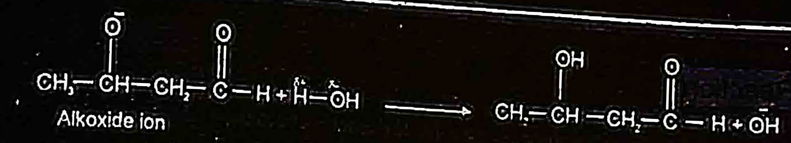
- **Formation of carbanion**
  The hydroxide ion acts as a base. It removes a proton from α-carbon of one molecule of the carbonyl compound to form a carbanion.



- **Attack of Nucleophile**
  The carbanion acts as a nucleophile. It attacks the electrophilic carbonyl carbon atom of the uncharged second molecule to form an alkoxide ion.



- **Protonation:**
  The alkoxide ion removes a proton from water to form aldol.



The basic catalyst hydroxide ion is regenerated.

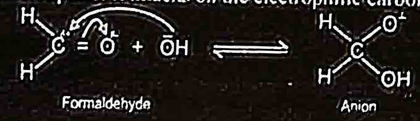
5. Cannizzaro's Reaction

- Aldehydes that have no α-hydrogen atoms undergo Cannizzaro's reaction.
- It is a disproportionation (self oxidation-reduction) reaction.
- Two molecules of the aldehyde are involved, one molecule being converted into the corresponding alcohol (the reduced product) and the other into the acid in the salt form (the oxidation product).
- The reaction is carried out with 50 percent aqueous solution of sodium hydroxide at room temperature.

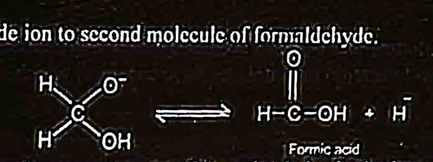


Mechanism

- **Step I:**
  The hydroxide ion acts as a nucleophile. It attacks on the electrophilic carbonyl carbon to form a complex anion.



- **Step II:**
  The anion transfers a hydride ion to second molecule of formaldehyde.

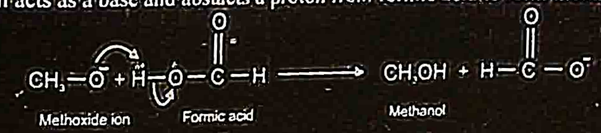


The presence of the negative charge on oxygen of the anion helps in the loss of hydride ion.

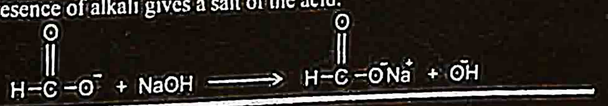
- **Step III:**



- **Step IV:**
  The methoxide ion acts as a base and abstacts a proton from formic acid to form methanol and formate ion.



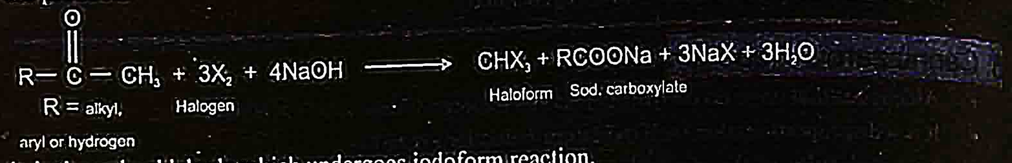
- **Step V:**
  The formate ion in the presence of alkali gives a salt of the acid.



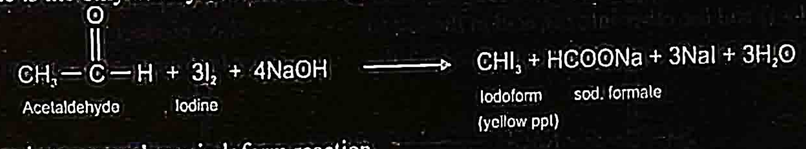
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6. Haloform Reaction

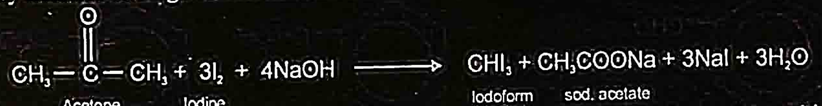
Only acetaldehyde and methyl ketones react with halogens in the presence of sodium hydroxide to give haloform and sodium salt of the acid. The term haloform is used for the reaction because a haloform (chloroform, bromoform or iodoform) is one of the products.



(i) Acetaldehyde is the only aldehyde which undergoes iodoform reaction.



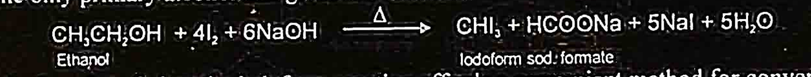
(ii) All secondary ketones undergo iodoform reaction.



(iii) Secondary alcohols containing the hydroxyl group on the second carbon atom also undergo this reaction.



(iv) Ethanol is the only primary alcohol that gives this reaction.



From a synthetic point of view the haloform reaction affords a convenient method for converting a methyl ketone to a carboxylic acid containing one carbon atom less than the parent compound.

Iodoform Test.

"The haloform reaction using iodine and aqueous sodium hydroxide is called the iodoform test." It results in the formation of water insoluble iodoform which is a yellow solid.

Use of Iodoform Test

- Iodoform test is used for distinguishing methyl ketones from other ketones.
- It is also used to distinguish ethanol form methanol and other primary alcohols.
- It can be used to distinguish acetaldehyde from other aldehydes.

MCQ's

Which of the following give positive iodoform test?

(a) 1 – Pentanol
(b) 2 – Pentanone
(c) 3 – Pentanone
(d) Pentanal

(B) ACID - CATALYSED ADDITION REACTIONS

The acid catalysed nucleophilic addition reaction will take place with a weak nucleophilic reagent. The addition is initiated by the proton (H^+) liberated by the acid. The proton combines with the carbonyl oxygen atom and increase the electorphilc character of the carbonyl carbon. As a result, the attack of the weaker nucleophile on the electrophilic carbon becomes easier.

The general mechanism of the reaction is as follows.

Step-I:



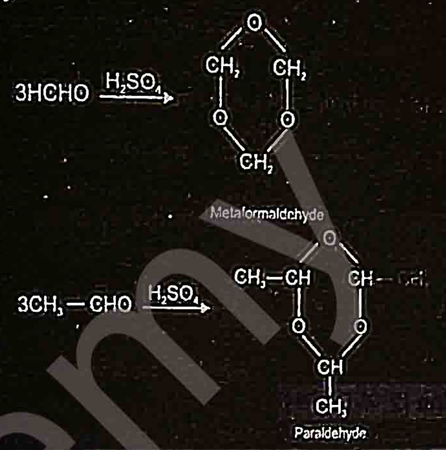
Step-II:



The acid-catalysed nucleophilic addition reactions of aldehydes and ketones are the following:

1. Polymerization of aldehydes

Both formaldehyde and acetaldehyde polymerize in the presence of dil. H_2SO_4 to give metaformaldehyde and paraldehyde respectively.



Metaformaldehyde is a white solid having melting point 62°C.

Paraldehyde is a cyclic trimer and is used as a hypnotic and soporific (sleep producing).

2. Reaction of Ammonia Derivatives

Aldehydes and ketones react with ammonia derivatives. $G - NH_2$ to form compounds containing the group. $>C = N - G$ and water. The reaction is known as condensation reaction or addition-elimination reaction because water is lost after addition occurs. The reaction is acid catalyzed.

The general reaction is:



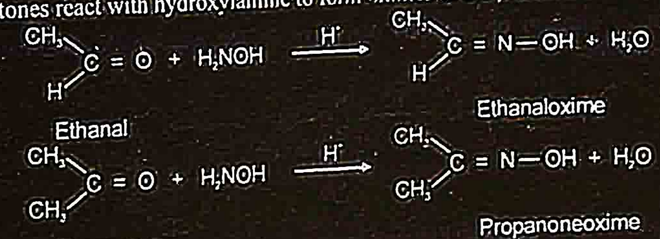
Where $G = \ddot{O}H, -\ddot{N}H_2, -\ddot{N}HC_6H_5, -\ddot{N}HCONH_2$, etc.

Some commonly used ammonia derivatives are hydroxylamine, NH_2OH, hydrazine, NH_2NH_2, phenylhydrazine, $C_6H_5NHNH_2$, semicarbazide, $NH_2NHCOHN_2$ and 2, 4, dinitrophenylhydrazine, $NH_2NHC_6H_3(NO_2)_2$.

The reactions of the above stated ammonia derivatives with aldehydes and ketones are as follow.

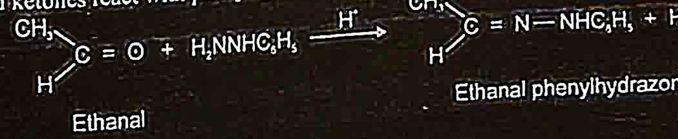
(i) Reaction with Hydroxylamine

Aldehyes and ketones react with hydroxylamine to form oximes in the presence of an acid.

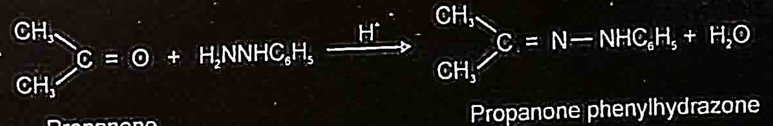


(ii) Reaction with Phenylhydrazine

Aldehydes and ketones react with phenylhydrazine to form phenylhydrazones in the presence of an acid.



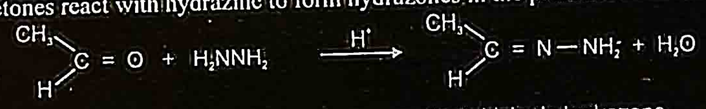
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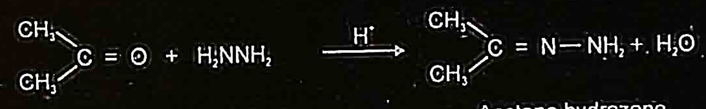
Propanone — Propanone phenylhydrazone

(iii) Reaction with Hydrazine

Aldehydes and ketones react with hydrazine to form hydrazones in the presence of an acid.



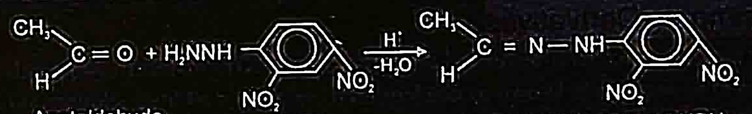
Acetaldehyde — Acetaldehyde hydrazone



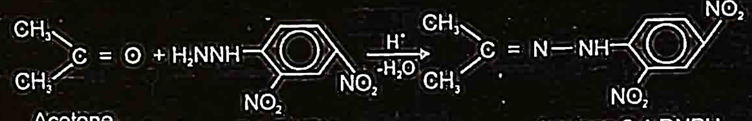
Acetone — Acetone hydrazone

(iv) Reaction with 2, 4-Dinitrophenylhydrazine [2, 4-DNPH]

Aldehydes and ketones react with 2, 4-dinitrophenylhydrazine to form 2, 4-dinitrophenylhyrazones in the presence of an acid.



Acetaldehyde — 2,4-DNPH — Acetaldehyde 2,4-DNPH



Acetone — 2,4-DNPH — Acetone 2,4-DNPH

The reactions can be used for the identification of aldehydes and ketones because 2, 4-dinitrophenylhydrazine are usually yellow or orange crystalline solids.

Mechanism of the Reaction of Ammonia Derivatives

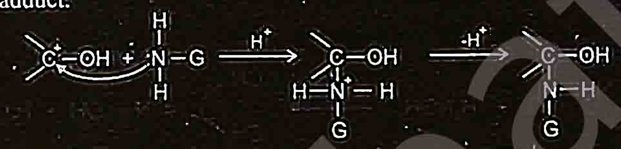
Step I:

Protonation of oxygen of the carbonyl group.



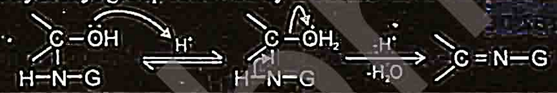
Step II:

Nucleophilic attack of nitrogen of ammonia derivative on the electrophilic positively charged carbon and deprotonation of the adduct.



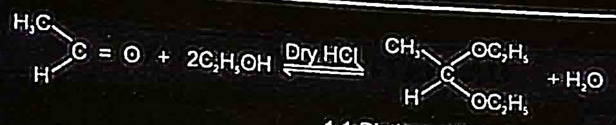
Step III:

Protonation of oxygen of hydroxyl group followed by the removal of water



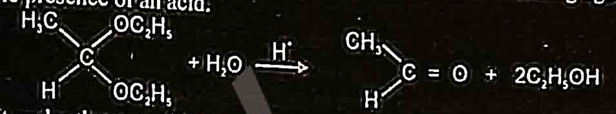
9. Addition of Alcohols

Aldehydes combine with alcohols in the presence of hydrogen chloride gas to form acetals. The hydrogen chloride gas acts as a catalyst. Both the alcohol and the hydrogen chloride gas must be dry.



1,1-Diethoxyethane (an acetal)

The reaction may be used to protect the aldehyde group against alkaline oxidizing agents. To regenerate aldehyde, the acetal is hydrolysed in the presence of an acid.



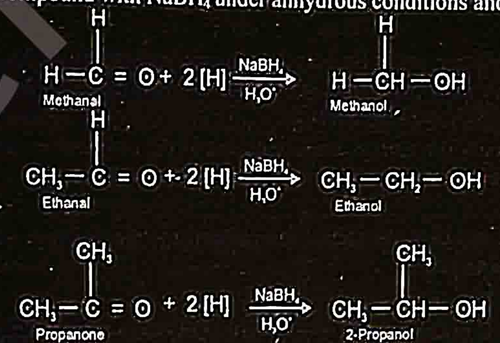
Ketones do not react under these conditions.

REDUCTION REACTIONS

Aldehydes and ketones can both be reduced. Aldehydes are reduced to primary alcohols whereas ketones to secondary alcohols. The carbonyl group is converted into an alcohol.

(i) Reduction with Sodium Borohydride

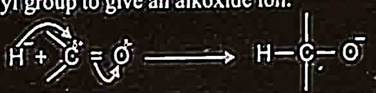
Aldehydes and ketones are reduced to alcohols with sodium borohydride, $NaBH_4$. The reaction is carried out in two steps: reaction of the carbon compound with $NaBH_4$ under anhydrous conditions and then hydrolysis.



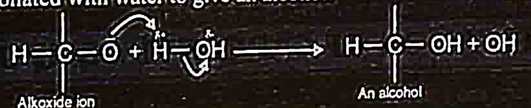
Sodium borohydride reduces the carbon-oxygen double bond but not the carbon-carbon multiple bond.

Mechanism

The tetrahydridoborate (III) ion BH_4^- is source of hydride ion, H^-. The hydride ion acts as a nucleophile. It attacks on the electrophilic carbon of the carbonyl group to give an alkoxide ion.

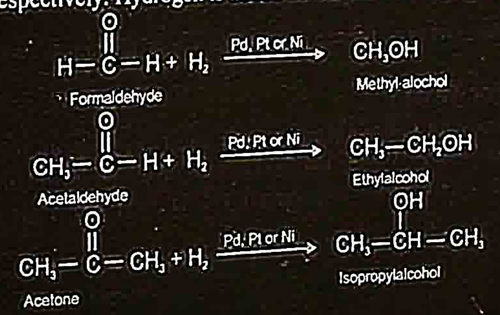


The alkoxide ion is protonated with water to give an alcohol.



(ii) Catalytic Reduction

Aldehydes and ketones on reduction with hydrogen in the presence of a metal catalyst like Pd, Pt, or Ni form primary and secondary alcohols respectively. Hydrogen is added across the carbonyl group.



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OXIDATION REACTIONS

(i) Oxidation of Aldehydes

- Aldehydes are easily oxidized by mild oxidizing agents like Tollen's reagent, Fehling's solution and Benedict's solution.
- They are oxidized to carboxylic acid by strong oxidizing agents such as $K_2Cr_2O_7/H_2SO_4$, $KMnO_4/H_2SO_4$ and dilute nitric acid.
- The hydrogen atom attached to the carbonyl group in aldehydes is oxidised to – OH group.

$$CH_3-\overset{O}{\overset{\|}{C}}-H + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Acetaldehyde → Acetic acid

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

Propionaldehyde → Propionic acid

Mild oxidizing agents	Strong oxidizing agents
• Tollen's reagent	• conc. HNO_3
• Fehling's solution	• $K_2Cr_2O_7/H_2SO_4$
• Benedict's solutions	• $KMnO_4/H_2SO_4$

The carboxylic acid has the same number of carbon atoms as are present in the parent aldehyde.

(ii) Oxidation of Ketones

- Ketones do not undergo oxidation easily because they require breaking of strong carbon-carbon bond.
- They give no reaction with mild oxidizing agent. They are only oxidized by strong oxidizing agents such as $K_2Cr_2O_7/H_2SO_4$, $KMnO_4/H_2SO_4$ and con. HNO_3.
- In oxidation of ketones, only the carbon atoms adjacent to the carbonyl group are attacked. The carbon atom joined to the smaller number of hydrogen atoms is preferentially oxidized.

Symmetrical ketones

In case of symmetrical ketones only one carbon atom adjacent to the carbonyl group is oxidized and a mixture of two carboxylic acids is always obtained.

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + 3[O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-OH + HCOOH$$

Acetone → Acetic acid + Formic acid

Unsymmetrical ketones

In case of unsymmetrical ketones, the carbon atom joined to the smaller number of hydrogen atom is preferentially oxidized and the carbonyl group remains with the smaller alkyl group.

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 + 3[O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-OH + CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Butanone → Acetic acid + Acetic acid

Q. What are factors which make aldehydes more reactive than ketones?

IDENTIFICATION OF CARBONYL COMPOUNDS

Detection tests for aldehydes and ketones.

1. 2, 4 DNPH Test:

Aldehyde and ketones form a yellow or red precipitate with 2, 4-dinitrophenylhdrazine solution.

2. Sodium Bisulphite Test:

Aldehydes and small methyl ketones form a crystalline white precipitate with saturated sodium bisulphite solution.

3. Tollen's Test [Silver Mirror Test] :

Aldehydes form silver mirror with Tollen's reagent (ammonical silver nitrate solution). Add Tollen's reagent to an aldehyde solution in a test tube and warm. A silver mirror is formed on the inside of the test tube.

$$AgNO_3 + 3NH_4OH \longrightarrow [Ag(NH_3)_2]OH + NH_4NO_3 + 2H_2O$$

$$R-CHO + 2[Ag(NH_3)_2]OH \longrightarrow R-COONH_4 + 2Ag + 2NH_3 + H_2O$$

Silver mirror

High quality mirrors are manufactured by using this principle. Ketones do not give this test.

4. Fehling's Solution Test [an alkaline solution containing a cupric tartrate complex ion]:

Aliphatic aldehydes form a brick-red precipitate with Fehling's solution. To an aldehyde solution, add Fehling's solution and boil. A brick red precipitate of cuprous oxide is formed. Ketones do not give this test..

$$R-CHO + 2Cu(OH)_2 + NaOH \longrightarrow R-COONa + Cu_2O + 3H_2O$$

Brick-red ppt

5. Benedict's Solution Test [an alkaline solution containing a cupric citrate complex ion]:

Aliphatic aldehydes form a brick-red precipitate with Benedict's solution. To an aldehyde solution, add Benedict's solution and boil. A brick-red precipitate of cuprous oxide is formed

$$RCHO + 2Cu(OH)_2 + NaOH \longrightarrow RCOONa + Cu_2O + 3H_2O$$

Brick-red ppt

Ketones do not give this test.

6. Sodium Nitroprusside Test:

Ketones produce a wine red or orange red colour on adding alkaline sodium nitroprusside solution drop wise. Aldehydes do not give this test.

Distinction Tests of Aldehydes and Ketones

Chemical reaction	Aldehyde	Ketone	Exception
Sodium bisulphito Test ($NaHSO_3$)	White ppt is formed	White ppt is formed	All aldehydes but only methyl ketones give this reaction
2, 4 DNPH Test (2, 4 - Dinitrophenylhydrazine)	Yellow Red ppt is formed	Yellow Red ppt is formed	Is used for both aldehydes and ketones
Tollen's Test Ammonical silver nitrate solution	A silver mirror (Ag) is formed	no reaction	Both aliphatic and aromatic aldehydes give this reaction but not ketones
Fehling's solution Test (An alkaline solution containing a cupric tartrate complex ion)	Brick Red ppt of Cu_2O is formed	no reaction	Aromatic aldehydes and ketones do not give this reaction
Benedict's solution Test (An alkaline solution containing a cupric citrate complex ion)	Brick Red ppt of Cu_2O is formed	no reaction	Aromatic aldehydes and ketones do not give this reaction
Sodium Nitroprusside Test $Na_4[Fe(CN)_5NO]$	no reaction	A wine red or Orange red colouration	Aldehydes do not give this reaction

(a) Uses of Fomaldehyde

(i) It is used in the manufacture of resins like urea-formaldehyde and plastics such as bakelite.
(ii) It is used in the manufacture of dyes such as indigo, para-rosaniline, etc.
(iii) Its 40% aqueous solution called formalin is used as an antiseptic, a disinfectant, a germicide, a fungicide and for preserving animal specimens and sterilizing surgical instruments.
(iv) It is used as a decolourising agent in vat dyeing.
(v) It is used in the silvering of mirrors.
(vi) It is used in making medicine urotropine used as a urinary antiseptic.
(vii) It is used in making formamint (formaldehyde + lactose) used as throat lozenges.
(viii) It is used in the processing of anti-poliovaccine.



Hexamethylene tetramine (Urotropine)

(b) Uses of Acetaldehyde

(i) It is used in the production of acetic acid, acetic anhydride, n-butanol, ethanol, 2-ethy-1-hexanol, vinyl acetate, paraldehyde, ethylacetate, etc.

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(ii) It is used to make acetaldehyde ammonia used as a rubber-accelerator.
(iii) It is used to make chloral hydrate, ehanol trimer and tetramer. Chloral hydrate and ethanol trimer are both used as hypnotic drugs whereas ethanol tetramer is used as a slug poison.
(iv) It is used as an antiseptic inhalent in nasal infections.
(v) It is used in silvering of mirrors.
(vi) It is used to make phenolic resins and synthetic drugs.

Conversion of formaldehyde into acetaldehyde

$$\underset{\text{Formaldehyde}}{HCHO} \xrightarrow[\text{Ether}]{CH_3MgI} C_2H_5OMgI \xrightarrow{H_2O} C_2H_5OH \xrightarrow[300^\circ C]{Cu} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

Conversion of acetaldehyde into formaldehyde

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH \xrightarrow{NaOH} CH_3COONa \xrightarrow[\text{Heat}]{\text{Sodalime}} CH_4 \xrightarrow[h\nu]{Cl_2} CH_3Cl \xrightarrow{AgOH} CH_3OH \xrightarrow[300^\circ C]{Cu} \underset{\text{Formaldehyde}}{HCHO}$$

KEY POINTS

1. Aldehydes and ketones contain the carbonyl group, C = O as the functional group.
2. Both aldehydes and ketones can be prepared by the oxidation of primary and secondary alcohols, respectively.
3. Both aldehydes and ketones undergo nucleophilic addition reactions. In these reactions, the negative part of the reagent combines with the electrophilic carbon of the carbonyl group whereas the positive part goes to the oxygen atom. They are base-catalysed addition reactions.
4. Two molecules of the same carbonyl compound condense to form an aldol. Aldehydes and ketones containing α–hydrogen atoms undergo this reaction in the presence of dilute sodium hydroxide.
5. Aldehydes that have no α–hydrogen atoms undergo Cannizzaro's reaction in the presence of concentrated sodium hydroxide.
6. Acetaldehyde and only methyl ketones react with halogens in the presence of sodium hydroxide to give haloform. It provides a useful method for converting a methyl ketone to a carboxylic acid containing one carbon atom less than the parent methyl ketone. Iodoform test is used for distinguishing methyl ketones from other ketones.
7. Aldehydes and ketones react with ammonia derivatives, $G - NH_2$ to form condensation products containing the group, $>C=N-G$ and water. The reaction is acid-catalysed.
8. Aldehydes and ketones are reduced to alcohols with sodium borohydride. Aldehydes and ketones are also reduced to alcohols with molecular hydrogen in the presence of catalyst like Pd, Pt or Ni.
9. Aldehydes are oxidized to carboxylic acids. $K_2Cr_2O_7$ in H_2SO_4 or $KMnO_4$ in H_2SO_4 may be used as the oxidizing agent. Ketones resist oxidation.
10. Aldehydes form silver-mirror with Tollen's reagent. Ketones do not give this test.
11. Aldehydes give a brick red precipitate with Fehling's solution on boiling.

SOLVED OBJECTIVE EXERCISE

Q1. Fill in the blanks.

(i) Aldehydes are the first oxidation product of _____
(ii) Ketones are the first oxidation product of_____
(iii) Aldehydes and ketones undergo__ addition reactions.
(iv) Formaldehyde reacts with _____ to give primary alcohol.

(v) Acetaldehyde reacts with _____ to give 2-butanol.
(vi) Aldehydes are strong _____ agents.
(vii) The oxidation of an _____ always gives a carboxylic acid.
(viii) The reduction of a _____always gives a secondary alcohol.
(ix) Formaldehyde gives _____test with Tollen's reagent.
(x) Acetaldehyde gives _____precipitates with Fehling's solution.

Answer Key.

(i)	Primary Alcohols	(ii)	Secondary Alcohols
(iii)	Nucleophilic	(iv)	Grignard Reagent
(v)	Ethyl magnesium bromide	(vi)	Reducing
(vii)	Aldehyde	(viii)	Ketone
(ix)	Silver Mirror	(x)	Brick red

Q2. Indicate True or false.

(i) Formaldehyde is used in the silvering of mirrors.
(ii) Ketones combine with alcohols in the presence of HCl gas to form acetals.
(iii) Acetaldehyde undergoes cannizzaro's reaction.
(iv) Formaldehyde is used for silvering of mirrors.
(v) Aldol condensation reaction is given by only those aldehydes and ketones which contain α-hydrogen atom.
(vi) Cannizzaro's reaction is given by only those aldehydes containing no α hydrogen atom.
(vii) Propanal and propanone behave differently with Tollen's reagent.
(viii) Acetone reacts with sodium bisulphite to give a yellow crystalline product.
(ix) Acetone on reduction gives a primary alcohol.
(x) 40%aqueous solutions of formaldehyde is called formalin.

Answer Key.

(i)	True	(ii)	False	(iii)	False	(iv)	True	(v)	True
(vi)	True	(vii)	True	(viii)	False	(ix)	False	(x)	True

Q3. Multiple choice questions. Encircle the correct answer.

(i) The carbon atom of a carbonyl group is.
(a) sp hybridized (b) sp^2 hybridized (c) sp^3 hybridized (d) none of these

(ii) Formalin is
(a) 10% solution of formaldehyde in water (b) 20% solution of formaldehyde in water
(c) 40% solution of formaldehyde in water (d) 60% solution of formaldehyde in water

(iii) Which of the following will have the highest boiling point?
(a) methanal (b) Ethanal (c) propanal (d) 2-Hexanone

(iv) Ketones are prepared by the oxidation of.
(a) primary alcohol (b) secondary alcohol (c) tertiary alcohol (d) none of these

(v) Acetone reacts with HCN to form a cyanohydrin. It is an example of.
(a) Electrophilic addition (b) Electrophilic substitution
(c) Nucleophilic addition (d) Nucleophilic substitution

(vi) Which of the following compounds will not give iodoform test on treatment with I_2 / NaOH
(a) Acetaldehyde (b) Acetone (c) butanone (d) 3-pentanone

(vii) which of the following compounds will react with Tollen's reagent.
(a) $CH_3-\overset{O}{\overset{\|}{C}}-H$ (b) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ (c) $CH_3-\overset{O}{\overset{\|}{C}}-OH$ (d) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

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(viii) Cannizzaro's reaction is not given by.
(a) formaldehyde (b) Acetaldehyde (c) Benzaldehyde (d) Trimethylacetaldehyde

(ix) Which of the following reagents will react with both aldehydes and ketones?
(a) Grignard reagent (b) Tollen's reagent (c) Fehling's reagent (d) Benedict's reagent

Solved Exercise MCQ's

Q. No.	Answer	Reason
(i)	(b) sp^2 hybridized	> C = O, double bond shows sp^2 character of carbonyl group.
(ii)	(c) 40% solution of formaldehyde in water	It is used as an antiseptic, a disinfectant, a germicide, a fungicide etc.
(iii)	(d) 2-Hexanone	2-Hexanone has highest b.p. due to large size.
(iv)	(b) secondary alcohols	$R-\underset{R}{\overset{}{CH}}-OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} R-\overset{O}{\overset{\|}{C}}-R + H_2O$
(v)	(c) Nucleophilic addition	As reaction starts by attack of nucleophile.
(vi)	(d) 3-Pentanone	In 3 – Pentanone, methyl group ($-CH_3$) is attached with carbonyl carbon, so it gives iodoform test.
(vii)	(a) $CH_3-\overset{O}{\overset{\|}{C}}-H$	Aldehyde form silver mirror with Tollen's reagent.
(viii)	(b) Acetaldehyde	Acetaldehyde (CH_3CHO) have α– hydrogen atom
(ix)	(a) Grignard reagent	Tollen, Fehling and Benedict's reagents do not react with ketones because they are not strong oxidizing agents.

Short Answers Questions

Q. How Cannizzaro's reaction is called self-oxidation and reduction reaction?

Ans: Cannizzaro's reaction is self-oxidation reduction reaction:

Cannizzaro's reaction is self-oxidation reduction reaction. Two molecules of the aldehyde are involved, one molecule being converted into the corresponding alcohol (the reduced product) and the other into the acid in the salt form (the oxidation product). The reaction is carried out with 50% aqueous solution of sodium hydroxide at room temperature.

$$2H-\overset{O}{\overset{\|}{C}}-H + NaOH \longrightarrow \underset{\text{Methyl alcohol}}{CH_3OH} + \underset{\text{Sodium formate}}{H-\overset{O}{\overset{\|}{C}}-O^-Na^+}$$

Q. What types of aldehydes give aldol condensation?

Ans: Aldehyde giving aldol Condensation:

Aldehydes possessing ∝-hydrogen atoms react with a cold dilute solution of an alkali to form addition products known as aldols. All the aldehydes give aldol condensation except those which have no ∝-hydrogen atoms.

Example:

$$\underset{\text{Ethanal}}{CH_3-\overset{O}{\overset{\|}{C}}-H} + \underset{\text{Ethanal}}{H-CH_2-\overset{O}{\overset{\|}{C}}-H} \xrightleftharpoons{\text{dil. NaOH}} \underset{\text{3-Hydroxybutanal (aldol)}}{CH_3-\underset{OH}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-H}$$

Q. What is silver mirror test?

Ans: Silver Mirror Test:

Aldehydes form silver mirror with Tollen's reagent (ammonical silver nitrate solution). Add Tollen's regent to an aldehyde solution in a test tube and warm. A silver mirror is formed on the inside of test tube.

$$AgNO_3 + 3NH_4OH \longrightarrow [Ag(NH_3)_2]OH + NH_4NO_3 + 2H_2O$$

$$R-CHO + 2[Ag(NH_3)_2]OH \longrightarrow \underset{\text{Silver mirror}}{R-COONH_4} + 2Ag + 2NH_3 + H_2O$$

Q. Name two mild oxidizing agents, which distinguish aldehydes and ketones.

Ans: Mild oxidizing agents:

The mild oxidizing agents are:

(i) Tollen's regent ($AgNO_3 + NH_4OH$)

(ii) Fehling's solution (an alkaline solution containing a cupric tartarate complex ion)

Aldehydes are easily oxidized by mild oxidizing agents while ketones do not oxidized by mild oxidizing agents.

Q. What are factors which make aldehydes more reactive than ketones?

Ans: Factors make aldehydes more reactive:

The reactivity of carbonyl compounds depends upon two factors:

(i) **Electrophilic character of carbonyl carbon:**
Alkyl groups are attached with carbonyl carbon in ketones. These alkyl groups donate electrons to carbon atom and decrease its electrophilic character. In this way its reactivity decreases as compared to aldehydes.

(ii) **Stearic Hindrance:**
In ketones, bulky alkyl groups create stearic hindrance in the attack of nucleophilic reagent. This makes it less reactive than aldehydes (having one hydrogen atom instead of alkyl groups)

Q.16 How would you bring about the following conversions?

(i)	Acetone into t-butyl alcohol	(ii)	Propanal into 1-propanol	(iii)	Propanone into 2-propanol
(iv)	methanal into ethanal	(v)	Ethanal into propanone	(vi)	Ethanal into 2-propanol
(vii)	Ethyne into ethanol	(viii)	Ethene into ethanal	(ix)	Ethanal into ethanol
(x)	Ethanol into 2-butanone	(xi)	Methanol into ethanal	(xii)	Ethanol into ethanoic acid

Ans:

(i) Acetone into t-butyl alcohol

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3MgBr \xrightarrow{\text{ether}} CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-O^-Mg^+Br$$

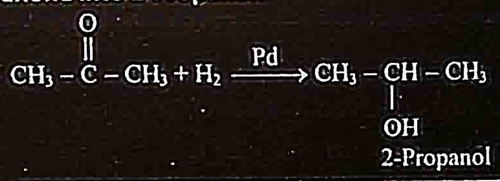
$$CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-O^-Mg^+Br \xrightarrow{H_3O^+} \underset{\text{t-butyl alcohol}}{CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-OH} + Mg\begin{matrix}Br\\OH\end{matrix}$$

(ii) Propanal into 1-Propanol

$$\underset{\text{Propanal}}{CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H} + H_2 \xrightarrow{Pd} \underset{\text{1-Propanol}}{CH_3-CH_2-CH_2-OH}$$

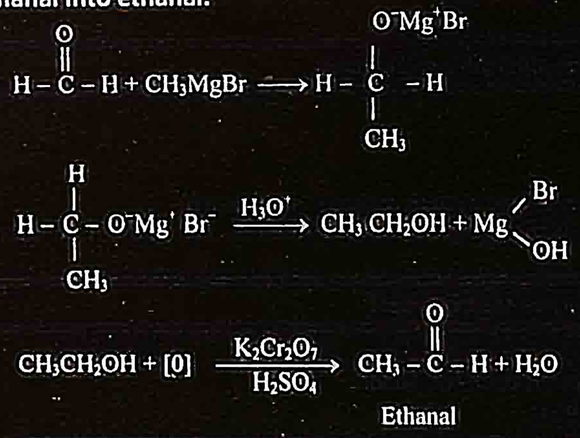
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(iii) Propanone into 2-Propanol:



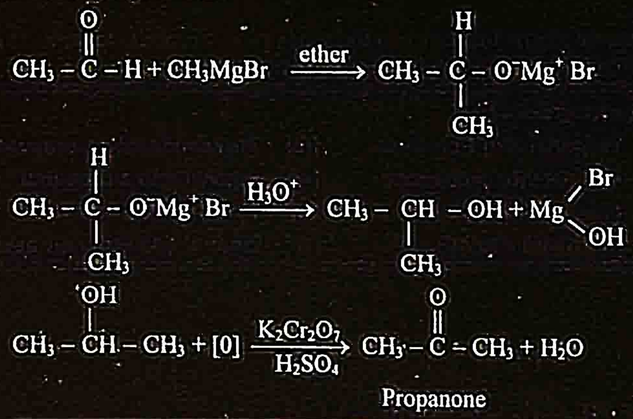
2-Propanol

(iv) Methanal into ethanal:



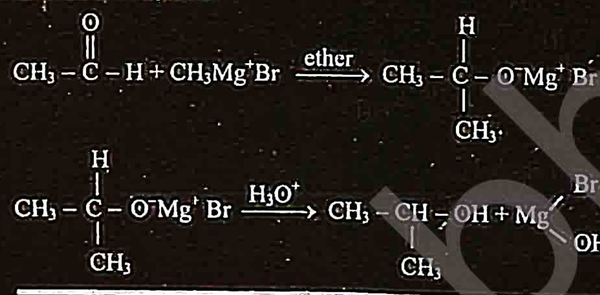
Ethanal

(v) Ethanal into propanone:

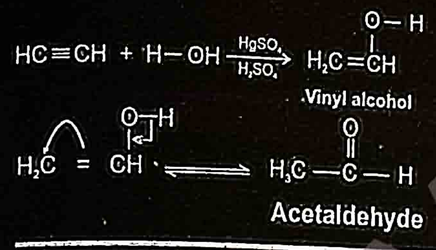


Propanone

(vi) Ethanal into 2-Propanol

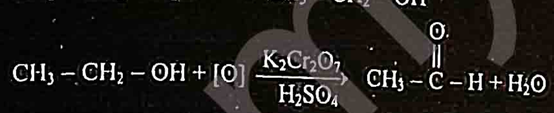


(vii) Ethyne into ethanal:

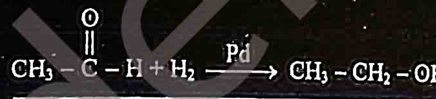


Acetaldehyde

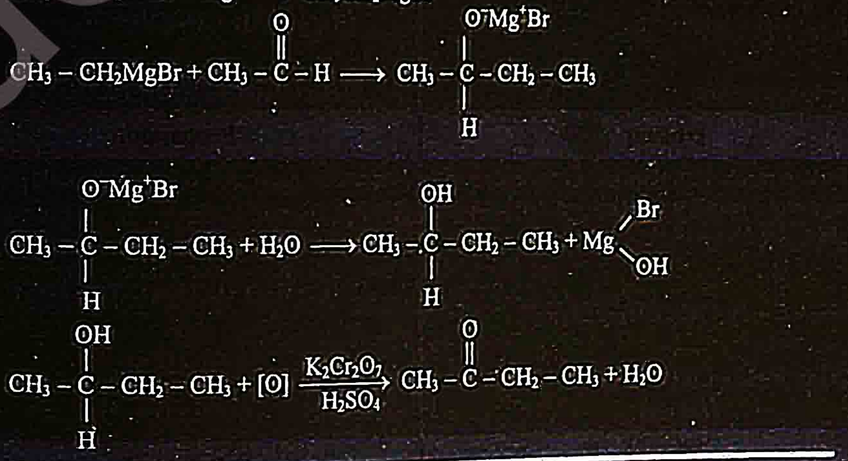
(viii) Ethene into ethanal:



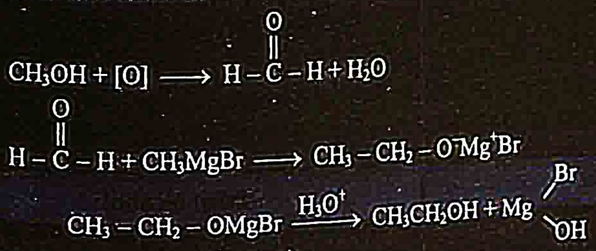
(ix) Ethanal into ethanol



(x) Ethanol into 2-Butanone



(xi) Methanol into ethanal:



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$$CH_3CH_2OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3 - \overset{O}{\overset{\|}{C}} - H + H_2O$$

(xii) Ethanol into ethanoic acid:

$$CH_3CH_2OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3 - \overset{O}{\overset{\|}{C}} - H + H_2O$$

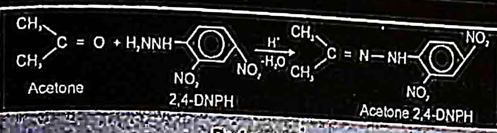
$$CH_3 - \overset{O}{\overset{\|}{C}} - H + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3 - \overset{O}{\overset{\|}{C}} - OH$$

Q.17 How will you distinguish between:

(i) Methanal and ethanal (ii) Ethanal and propanone (iii) Ethanal and propanal
(iv) Acetone and ethyl alcohol (v) Butanone and 3-Pentanone (vi) Acetaldehyde and benzaldehyde
(vii) 2-Pentanone and 3-Pentanone

Ans: Distinguish between:

(i)	**Methanal**	**Ethanal**
	It does not give iodoform test. $H - \overset{O}{\overset{\|}{C}} - H + NaOH + I_2 \rightarrow$ No Iodoform test.	It gives iodoform test. $CH_3 - \overset{O}{\overset{\|}{C}} - H + 4NaOH + 3I_2 \rightarrow CHI_3 + 3NaI + 3H_2O + HCOONa$
(ii)	**Ethanal**	**Propanone**
	Ethanal when reacts with mild oxidizing agents like Benedict's and Fehling's solution we get brick red precipitate. $CH_3 - \overset{O}{\overset{\|}{C}} - H + 2Cu(OH)_2 + 2NaOH \rightarrow CH_3COONa + Cu_2O + 3H_2O$ (red ppt)	Propanone does not react with mild oxidizing agents. $CH_3 - \overset{O}{\overset{\|}{C}} - CH_3 + Cu(OH)_2 + NaOH \rightarrow$ No reaction
(iii)	**Ethanal**	**Propanal**
	Ethanal gives iodoform test. $CH_3 - \overset{O}{\overset{\|}{C}} - H + 4NaOH + 3I_2 \rightarrow CHI_3 + 3NaI + 3H_2O + HCOONa$	Propanal does not give iodoform test. $CH_3 - CH_2 - \overset{O}{\overset{\|}{C}} - H + NaOH + I_2 \rightarrow$ No reaction.
(iv)	**Acetone**	**Ethyl alcohol**
	Acetone reacts with 2, 4-dinitrophenyhydrazine to form 2, 4-dinitrophenylhyrazones in the presence of an acid.	Ethyl alcohol forms an oily layer with $ZnCl_2/HCl$ on heating. $CH_3CH_2OH + HCl \xrightarrow[Heat]{ZnCl_2} CH_3CH_2Cl + H_2O$



(v)	**Butanone**	**3-Pentanone**
	Butanone gives iodoform test. $CH_3 - CH_2 - \overset{O}{\overset{\|}{C}} - CH_3 + 4NaOH + 3I_2 \rightarrow CH_3 - CH_2COONa + 3NaI + CHI_3 + 3H_2O$	It does not gives iodoform test. $CH_3 - CH_2 - \overset{O}{\overset{\|}{C}} - CH_2 - CH_3 + NaOH + I_2 \rightarrow$ No reaction
(vi)	**Acetaldehyde**	**Benzaldehyde**
	It gives iodoform test. $CH_3 - \overset{O}{\overset{\|}{C}} - H + 4NaOH + 3I_2 \rightarrow CHI_3 + 3NaI + 3H_2O + HCOONa$	It does not give iodoform test $C_6H_5 - \overset{O}{\overset{\|}{C}} - H + NaOH + I_2 \rightarrow$ No reaction
(vii)	**2-Pentanone**	**3-Pentanone**
	2-Pentanone gives iodoform test. $CH_3 - CH_2 - CH_2 - \overset{O}{\overset{\|}{C}} - CH_3 + 4NaOH + 3I_2 \rightarrow CH_3 - CH_2 - CH_2COONa + CHI_3 + 3NaI + 3H_2O$	3-Pentanone does not give iodoform test. $CH_3 - CH_2 - \overset{O}{\overset{\|}{C}} - CH_2 - CH_3 + NaOH + I_2 \rightarrow$ No reaction

Previous Board Questions

1. How will you convert ethanal into ethanol, give equation?
2. Give the reactions of: (a) Acetaldehyde (b) Acetone with I_2 / NaOH
3. Give the mechanism of addition of HCN to Acetone.
4. Write down the formula and IUPAC name of an acetal.
5. Write down any four uses of formaldehyde.
6. How formaldehyde reacts with: (i) Tollen's reagent (ii) Fehling solution
7. Describe reduction of Acetone with: (i) $NaBH_4$ / H_2O (ii) H_2 /Pd
8. What types of Aldehydes give Cannizzaro reaction?
9. Discuss reduction of Aldehydes with: (a) $NaBH_4$ / H_2O (b) H_2 / Pd
10. Give industrial method with all the conditions to produce formaldehyde.
11. How an aldehyde is distinguished from a ketonic by Fehling's solution test? Write the equation as well.
12. Give equations for reaction of phenylhdrazine with the following
    (a) Ethanal (b) Propanone
13. What type of polarity is present in Carbonyl group?
14. Name oxidizing agents which can oxidize aldehydes but not the ketones?
15. Write down the uses of acetaldehyde.
16. How acids and bases acting as catalysts increase the reactivity of aldehydes and ketones?
17. How aldehydes react with alcohols to give hemiacetals and acetals?

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18. What is Sodium Nitroprusside test?
19. What products are obtained by the reduction of acetaldehyde and acetone with $NaBH_4$?
20. How formalin is prepared on the commercial scale from methyl alcohol?
21. Why Tollen's test is also called silver mirror test?
22. How does acetaldehyde react with HCN and C_2H_5MgI?
23. Discuss the chemistry of Tollen's test.
24. What is condensation reaction? Give an example.
25. Give the mechanism of Cannizzaro's reaction.

For Answers see
Scholar's CHEMISTRY (Objective) XII
AVAILABLE IN MARKET BY THE SAME AUTHORS
Mcq's, Additional Short Questions with Answers
Previous Board papers
With ENTRY TESTS MCQ's
And
Many More in the Objective Chemistry

ATP
Alternative To Practical
ON
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فیڈرل بورڈ کے نصاب اور نئے طریقہ کار کے عین مطابق
فیڈرل
(لازمی)
سہ ماہیہ اردو
معروضی و موضوعی نئے قواعد
حصہ اول
برائے گیارھویں جماعت
پروفیسر ڈاکٹر شیر علی

Subjective:

Physics	Part I & II	Features
Chemistry	Part I & II	Simple approach To Text with Side Information
Biology	Part I & II	MCQ's Answers With Hints
Mathematics	Part I & II	Solved Exercises
		Additional Information
Objective:		Previous Board Questions & MCQ's
Physics	Part I & II	Solved Examples
Chemistry	Part I & II	Numerical Problems
Biology	Part I & II	Conceptual MCQ's (*For Entry Test*) in Objectives
Mathematics	Part I & II	

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CHAPTER 13

CARBOXYLIC ACIDS

Introduction

"Organic compounds containing ($-\overset{O}{\overset{\|}{C}}-OH$) as a functional group are called carboxylic acids."

The – COOH group which itself is made up of a carbonyl group ($>C=O$) and a hydroxyl group (– OH) is called a carboxyl group (Carb from carbonyl and oxyl from hydroxyl).

Classification of Carboxylic acids

(A) On the basis of side chain

(i) Aliphatic carboxylic acids: "Carboxylic acids in which carboxyl group (– COOH) is attached with alkyl group are called aliphatic carboxylic acids."

General Formula:

$R-\overset{O}{\overset{\|}{C}}-OH$ Where R = H or an alkyl group.

Examples

$H-\overset{O}{\overset{\|}{C}}-OH$ Methanoic acid or Formic acid

$CH_3-\overset{O}{\overset{\|}{C}}-OH$ Ethanoic acid or Acetic acid

(ii) Aromatic carboxylic acids: "Carboxylic acids in which carboxyl group (– COOH) is attached with aryl group are called aromatic carboxylic acids."

General Formula

$Ar-\overset{O}{\overset{\|}{C}}-OH$ Where Ar is a phenyl or an aryl group

Examples



Benzoic acid



1,2-Benzenedicarboxylic acid or Phthalic acid

(B) On the basis of number of carboxyl groups

Carboxylic acids are further classified as mono, di, tri, or poly carboxylic acids as they contain one, two, three, or many carboxyl groups respectively in their molecules.

(i) Aliphatic Monocarboxylic acids
(ii) Aliphatic Dicarboxylic acids
(iii) Aromatic Monocarboxylic acids
(iv) Aromatic Dicarboxylic acids

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Aliphatic Monocarboxylic Acids

Chemical formula	Common name	IUPAC name
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3(CH_2)_2COOH$	Butyric acid	Butanoic acid
$CH_3(CH_2)_3COOH$	Valeric acid	Pentanoic acid
$CH_3(CH_2)_4COOH$	Caproic acid	Hexanoic acid
$CH_3(CH_2)_{14}COOH$	Palmitic acid	Hexadecanoic acid
$CH_3(CH_2)_{16}COOH$	Stearic acid	Octadecanoic acid
$C_{17}H_{33}COOH$	Oleic acid	9 - Octadecenoic acid

Aliphatic Dicarboxylic Acids

Chemical formula	Common name	IUPAC name
$(COOH)_2$	Oxalic acid	Ethane 1, 2 - dioic acid
$HOOC-CH_2-COOH$	Malonic acid	Propane 1, 3-dioic acid
$HOOC-(CH_2)_2-COOH$	Succinic acid	Butane 1, 4-dioic acid
$HOOC-(CH_2)_3-COOH$	Glutaric acid	Pantane 1, 5-dioic acid
$HOOC-(CH_2)_4-COOH$	Adipic acid	Hexane 1, 6-dioic acid
HC—COOH ‖ HC—COOH (Cis form)	Maleic acid	Cis Butendioic acid
HC—COOH ‖ HC—COOH (Trans form)	Fumeric acid	Trans Butendioic acid

Aromatic monocarboxylic acid



Benzoic acid

Aromatic dicarboxylic acids



1, 2 - Benzenedicarboxylic acid (Phthalic acid)



1, 3 - Benzenedicarboxylic acid (Iso-phthalic acid)



1, 4 - Benzenedicarboxylic acid (Tere - phthalic acid)

Nomenclature of Carboxylic Acids

Q7. (a) What are fatty acids?

Fatty acids

The aliphatic monocarboxylic acids are commonly called **fatty acids** because higher members of this series such as palmitic acid ($C_{15}H_{31}COOH$), stearic acid ($C_{17}H_{35}COOH$), etc. are obtained by the hydrolysis of fats and oils.

The aliphatic monocarboxylic acids may be given common names or IUPAC names.

Common or Trivial names

The common names of carboxylic acids were derived from the source from which they are isolated.

- The irritation caused by an ant bite is due to formic acid (Latin word formica, ant). It was first isolated by the distillation of red ants.
- Similarly acetic acid was first isolated from vinegar.
- Butyric acid was named after butyrum means butter.

The IUPAC Nomenclature

- The IUPAC names of saturated monocarboxylic acids are alkanoic acids.
- These are derived from the names of the alkanes containing the same number of carbon atoms as the acid.
- The ending "-e" of the alkane name is dropped and suffix-oic acid is added.
- Thus, acetic acid gets the name ethanoic acid.

The position of substituents are indicated by Arabic numerals with the carboxyl group given number 1 as shown below:

$$^{4}C-{}^{3}C-{}^{2}C-{}^{1}C(=O)-OH$$

The common and IUPAC names of the some common monocarboxylic acids are given in the table below.

Structural Formula	Common Name	IUPAC Name
H—COOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3-CH_2-COOH	Propionic acid	Propanoic acid
$CH_3-CH_2-CH_2-COOH$	Butyric acid	Butanoic acid
$CH_3-CH(CH_3)-COOH$	iso–Butyric acid	2–Methyl propanoic acid

GENERAL METHODS OF PREPARATION

There are following methods for the preparation of carboxylic acids,

1. From Primary Alcohols and Aldehydes

Primary alcohols and aldehydes are readily oxidized to corresponding carboxylic acids by oxidizing agents such as potassium dichromate in an acidic medium.

$$\underset{\text{Primary alcohol}}{R-CH_2-OH}+[O]\xrightarrow[H_2SO_4]{K_2Cr_2O_7}\underset{\text{aldehyde}}{R-CHO}\xrightarrow{[O]}\underset{\text{Carboxylic acid}}{RCOOH}$$

$$\underset{\text{Ethanol}}{CH_3-CH_2-OH}+[O]\xrightarrow[H_2SO_4]{K_2Cr_2O_7}\underset{\text{Ethanal}}{CH_3-C(=O)-H}\xrightarrow{[O]}\underset{\text{Ethanoic acid}}{CH_3COOH}$$

Aldehydes are easily oxidized to corresponding carboxylic acids even by mild oxidizing agents such as Tollen's Reagent (Ammoniacal silver nitrate).

$$\underset{\text{Ethanal}}{CH_3-CHO}+[O]\longrightarrow\underset{\text{Ethanoic acid}}{CH_3COOH}$$

2. From Alkanenitriles

Nitriles: Compounds having a cyanide (—C ≡ N) group are called nitriles.

CH_3CN = Ethanenitrile, C_2H_5CN = Propanenitrile (R – CN = Alkanenitrile)

Preparation of Alkanenitriles: Alkanenitriles can be prepared by treating alkyl halide with alcoholic potassium cyanide.

$$R-X+KCN\xrightarrow{\text{Alcohol}}R-CN+KX$$

Hydrolysis of Alkanenitriles: Hydrolysis of an alkane nitrile on boiling with mineral acids or alkalis yields corresponding carboxylic acid.

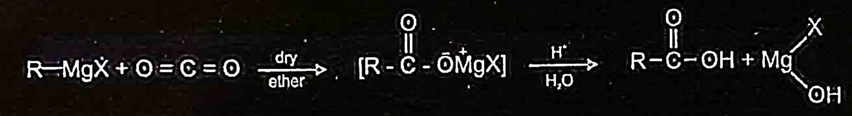
$$R-C\equiv N+2H_2O\xrightarrow{H^+\text{ or }OH^-}RCOOH+NH_3$$

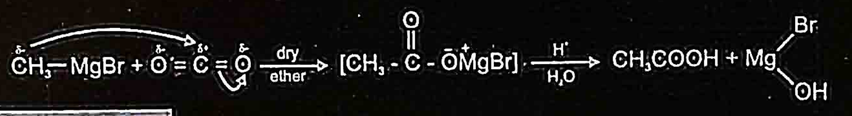
$$CH_3C\equiv N+2H_2O+HCl\longrightarrow CH_3COOH+NH_4Cl$$

It may be noted that acid produced has one carbon atom more than the original alkyl halide.

3. From Grignard Reagent

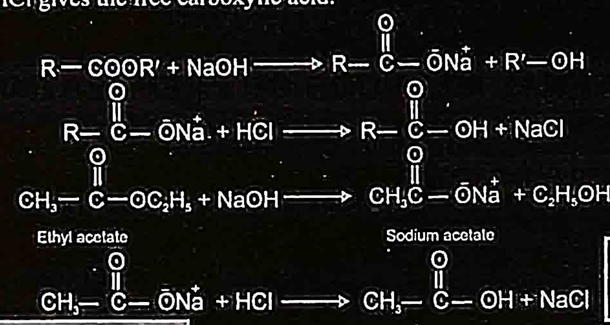
Carboxylic acids can be prepared by the action of Grignard reagent with carbon dioxide. This reaction is either carried out by passing carbon dioxide through the ethereal solution of corresponding Grignard reagent or by adding Grignard reagent to crushed dry ice suspended in ether. The addition product on reaction with a mineral acid produces carboxylic acid.





4. By the Hydrolysis of Esters

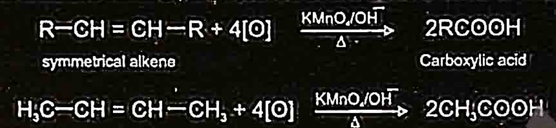
The appropriate ester on boiling with concentrated sodium hydroxide yields sodium salt of the acid. This resulting salt when treated with dilute HCl gives the free carboxylic acid.



Q. How would you convert 2–Butene to acetic acid?

5. By the Oxidative Cleavage of Alkenes

Alkenes when heated with alkaline $KMnO_4$ are cleaved at the double bond to form carboxylic acids.



Physical Characteristics

(i) Smell

The first three aliphatic acids *i.e.*, formic acid, acetic acid and propionic acid are colourless liquids and have pungent smell. The next three acids C_4 to C_6 are colourless liquids with somewhat unpleasant smell.

(ii) Solubility

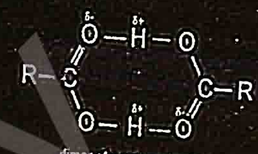
Among the aliphatic acids, the first four members are very soluble in water due to hydrogen bonding.



The solubility in water gradually decreases with the increase in molecular mass.

(iii) Boiling Points

The boiling points of carboxylic acids are relatively high due to intermolecular hydrogen bonding. The molecular mass determination in non-polar solvents like benzene shows that carboxylic acids exist as cyclic dimer.



Examples

HCOOH	CH_3COOH	C_2H_5COOH
373K (100°C)	391K (118°C)	424K (141°C)

(iv) Melting Points

The melting points of carboxylic acids increase irregularly with the increase in molecular mass. It has been observed that the melting points of carboxylic acids containing even number of carbon atoms are higher than the next lower and higher members containing odd number of carbon atoms.

Examples

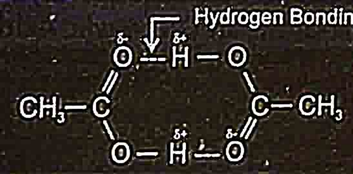
	CH_3CH_2COOH (3 carbon)	$CH_3CH_2CH_2COOH$ (4 carbon)	$CH_3CH_2CH_2CH_2COOH$ (5 carbon)
Melting points	251K(-22°C)	267K(-6°C)	237K(-36°C)

Q. Why the molecular masses of carboxylic acids become double in non polar solvent?

Ans. The molecular mass determination of carboxylic acids in non polar solvents like benzene shows that they exist as cyclic dimers due to intermolecular hydrogen bonding. So, due to formation of cyclic dimers, they show double molecular mass.

Example:-

The molecular mass of acetic acid is 60 amu, but in benzene, it is 120 amu. This is due to the formation of cyclic dimer.



Dimer of acetic acid

MCQ's The weakest acid among the following is

(a) CH_3COOH (b) $ClCH_2COOH$ (c) $Cl_2CHCOOH$ (d) Cl_3CCOOH

Points to be Noted:

i) As the length of carbon chain increases, the acidic strength of carboxylic acids decreases.

ii) The acidity of carboxylic acids increases as the number of electron with drawing group (F, Cl, Br, NO_2 etc) increases in the α position

Reactivity of Carboxyl Group

The carboxyl group displays the chemistry of both the carbonyl and the hydroxyl groups. In most reactions of carboxylic acids the carboxyl group is retained however, the reactivity of these molecules is a consequence of the presence of the carbonyl group.

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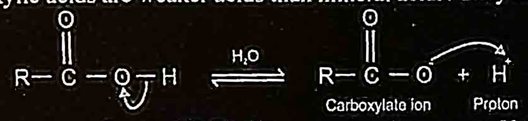
Reactions of Carboxylic Acids

Carboxylic acids undergo the following type of reactions.

(a) The reactions in which hydrogen atom of the carboxyl group is involved (salt formation).
(b) The reactions in which OH group is replaced by another group.
(c) The reactions involving carboxyl group as a whole.

(a) Reaction Involving H Atom of the Carboxyl Group

Carboxylic acids are weaker acids than mineral acids. They furnish H^+ when dissolved in water.



In the presence of water (H_2O), the proton breaks away as H_3O^+ ion.

1. Reaction with Base

Carboxylic acids react with bases (NaOH, KOH) to form salts

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

Acetic acid — Sodium acetate

2. Reaction with Carbonates and Bicarbonates

Carboxylic acid decompose carbonates and bicarbonates evolving carbon dioxide gas with effervescence.

$$2CH_3COOH + Na_2CO_3 \longrightarrow 2CH_3COO^-Na^+ + CO_2 + H_2O$$

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COO^-Na^+ + CO_2 + H_2O$$

MCQ's
Acids form sodium salt, with the evolution of CO_2 on treatment with
(a) Sodium carbonate
(b) Sodium hydroxide
(c) Soda lime (d) Sodium metals

3. Reaction with Metals

Carboxylic acids react with active metals (Na, K, Ca, Mg etc.) to form their salts with the evolution of hydrogen gas.

$$2CH_3COOH + 2Na \longrightarrow 2CH_3COO^-Na^+ + H_2$$

(b) Reaction Involving the –OH Group of Carboxylic Acids

The carboxylic acid contains (– COOH) functional group, and like the carbonyl group of aldehydes and ketones, is susceptible to attack by a nucleophile. The addition of a nucleophile to the carboxyl group is always followed by the displacement of the –OH group by some other group, producing a carboxylic acid derivative. The –OH group can thus be replaced by X, OR and NH_2 to form halides, esters and amides respectively.

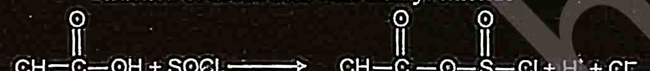
1. Reaction with Phosphorus pentachloride (PCl_5) and Thionyl Chloride ($SOCl_2$):

(a) $CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$

(b) $CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2 + HCl$

Mechanism

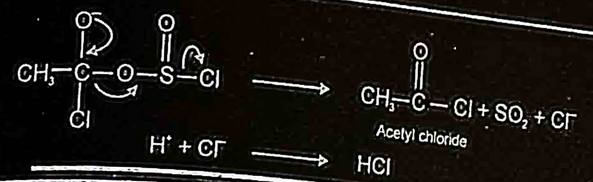
- Reaction of acetic acid with thionyl chloride

(i) 

- Attack of chloride on electrophilic carbon

(ii) 

- Removel of cholride and sulphur dioxide

(iii) 

$$H^+ + Cl^- \longrightarrow HCl$$

2. Formation of an Ester

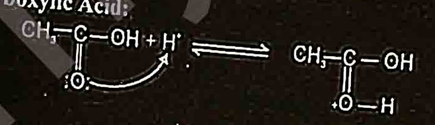
When carboxylic acids are heated with alcohols in the presence of concentrated H_2SO_4, esters are formed.

$$CH_3COOH + C_2H_5OH \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} CH_3COOC_2H_5 + H_2O$$

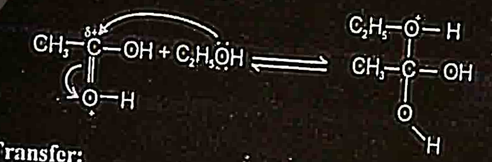
Mechanism

The various steps of the above reactions are as follows:

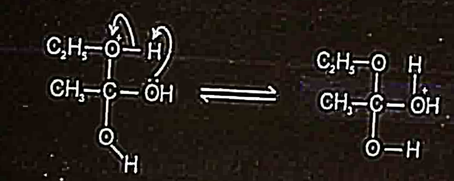
- **Protonation of Carboxylic Acid:**



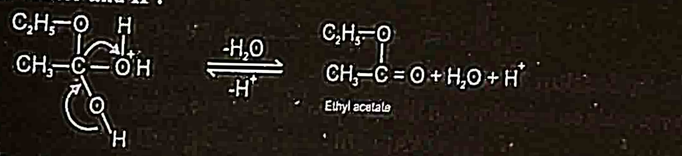
- **Attack of CH_3–CH_2OH:**



- **Hydrogen Ion Transfer:**



- **Elimination of Water and H^+:**



Esters have fruity smell and are used as artificial flavours. Flavours of some esters are listed in the table.

Ester	Flavour	Ester	Flavour
Amyl acetate	Banana	Isobutyl formate	Raspberry
Benzyl acetate	Jasmine	Ethyl butyrate	Pine apple
Amyl butyrate	Apricot	Octyl acetate	Orange

3. Formation of Amide (Reaction with ammonia)

Carboxylic acids react with ammonia to form ammonium salts which on heating produce acid amides.

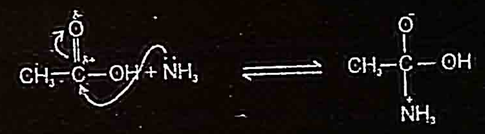
$$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4$$

$$CH_3COO^-\overset{+}{N}H_4 \xrightarrow[215°C]{Heat} CH_3CONH_2 + H_2O$$

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Mechanism

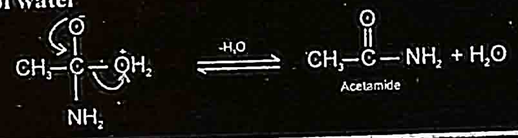
- Attack of NH_3 on acetic acid

(i) 

- Shifting of proton

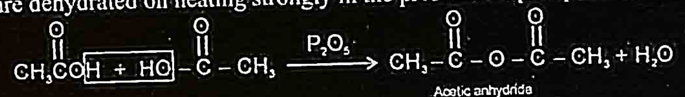
(ii) 

- Removal of water

(iii) 

4. Formation of Acid Anhydride

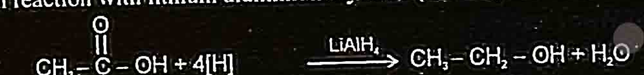
Carboxylic acids are dehydrated on heating strongly in the presence of phosphorus pentaoxide.



(c) Reactions Involving Carboxyl Group

(i) Partial Reduction to Alcohols

Carboxylic acids on reaction with lithium aluminium hydride ($LiAlH_4$) are reduced to alcohols.



(ii) Complete Reduction to Alkanes

Carboxylic acids on reduction with HI and red phosphorus give alkanes.



In this reaction –COOH group is reduced to a $-CH_3$ group.

Q. How would you convert:
(i) Carboxylic acids into alcohols (ii) Carboxylic acids into alkanes

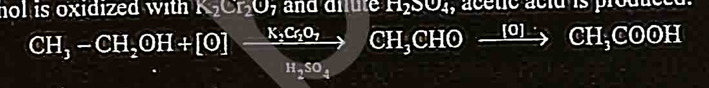
ACETIC ACID

It is most important carboxylic acid. Its dilute solution is known as vinegar. Acetic acid can be prepared by any of the general methods described earlier.

Laboratory Methods

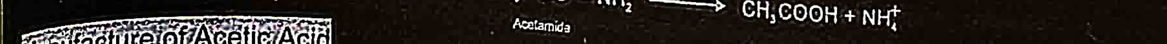
1. By the Oxidation of Ethyl Alcohol or Acetaldehyde

When ethyl alcohol is oxidized with $K_2Cr_2O_7$ and dilute H_2SO_4, acetic acid is produced.



2. By the Hydrolysis of Ethanenitrile

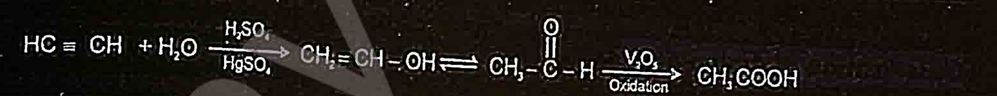
Ethanenirtile on hydrolysis with dilute HCl, gives acetic acid through acetamide.



Manufacture of Acetic Acid

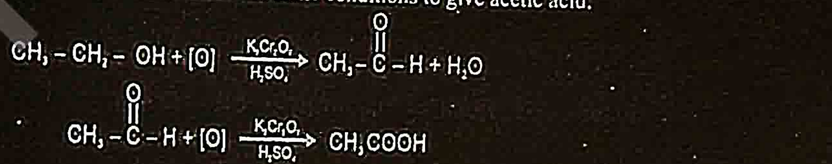
1. From Acetylene

Acetylene is treated with 20% H_2SO_4 and 1.0% $HgSO_4$ at 80°C to give ethanal (acetaldehyde) which is then oxidised using V_2O_5 to give acetic acid.



2. From Fermentation

Acetic acid is also prepared commercially by the oxidatioin of ethyl alcohol. Ethyl alcohol can be commercially prepared from molassess by a process called fermentation. It is oxidized by potassium dichromate in the presence of conc. H_2SO_4 to give acetaldehyde which is further oxidized under the same conditions to give acetic acid.



Physical Characteristics

Colour: Acetic acid is a colourless liquid with a boiling point 118°C.

Odour and taste: It has a strong vinegar like odour and sour taste.

Freezing Point: The pure acid freezes to an ice like solid at 17°C, therefore, it is called glacial acetic acid.

Solubility: It is miscible with water, alcohols and ether in all proportions.

Reactions of Acetic Acid

Chemical reactions of acetic acid have already been discussed in the general properties of the carboxylic acids.

Uses of Acetic Acid

Acetic acid is used:

(i) as a coagulant for latex in rubber industry.
(ii) in the manufacture of plastics (polyvinyl acetate), rayon (cellulose acetate) and silk.
(iii) in medicine as a local irritant.
(iv) as a solvent in the laboratory for carrying out reactions.
(v) in the manufacture of pickles.
(vi) in the manufacture of many organic compounds like acetone, acetates and esters.

AMINO ACIDS

"Amino acids are organic compounds containing both amino and carboxyl groups."

General formula:



- R is diffcrent for different amino acids.

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- The amino group may be present at any carbon atom other than that of the carboxyl group (–COOH). They are referred to as α, β, γ depending upon whether the amino group is present on the α, β, γ carbon atom relative to the carboxyl group.
- Almost all the naturally occurring amino acids are α–amino acids.
- The amino acids are very important because they are the building blocks of proteins. Proteins are very important for us.
- About twenty amino acids have been identified as the constituents of most of the animal and plant proteins.

Classification of Amino Acids

Q11. What are amino acids? Explain their different types with one example in each case.

(a) On the basis of nature

(i) Acidic amino acids:

"The amino acids which contain two carboxyl groups are called acidic amino acids."

Examples:

Aspartic acid $HOOC-CH_2-CH(NH_2)-COOH$

Glutamic acid $HOOC-CH_2-CH_2-CH(NH_2)-COOH$

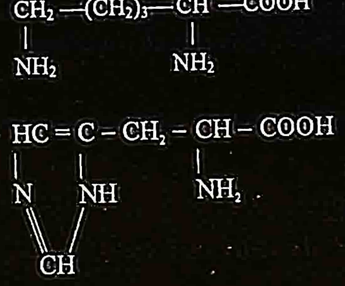
(ii) Basic amino acids:

"The amino acids which contain two amino groups are called basic amino acids."

Examples:

Lysine $CH_2(NH_2)-(CH_2)_3-CH(NH_2)-COOH$

Histidine



(iii) Neutral amino acids:

"Those amino acids which contain equal number of amino and carboxyl groups are called neutral amino acids."

Examples:

Glycine $CH_2(NH_2)-COOH$

Alanine $CH_3-CH(NH_2)-COOH$

(b) On the basis of necessity

On the basis of necessity, there are two classes of amino acids:

(a) Essential amino acids

"The amino acids which body cannot synthesize are called essential amino acids."

The essential amino acids must be supplied to our bodies through our diet for proper health and growth. They are ten (10) in numbers

Examples:

Lysine, Valine, Histidine, arginine etc.

Complete diet

A diet which provides all essential amino acids is called complete diet. e.g., Fish, egg & meat.

(b) Non-essential amino acids

"Those amino acids which body can synthesize are called non essential amino acids."

These amino acids are not required by our bodies from any external source. They are ten (10) in number.

Examples

Glycine, Alanine, Proline etc.

Nomenclature of Amino Acids

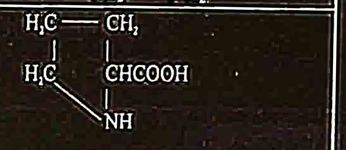
(i) Although amino acids can be named according to IUPAC system, they are generally known by their trivial names. These trivial names usually reflect the origin or an obvious property of the compound.

Examples: Glycine, is so named, because it has a sweet taste (Greek glykys-sweet). Tyrosine was first isolated form cheese (from Greek tyros-cheese).

(ii) For the sake of simplicity, each amino acid has been given an abbreviation which generally consists of the first three letters of the common name.

Examples: The simplest amino acid is glycine which may be abbreviated as Gly. Similarly, alanine may be represented as Ala.

Names, structural formulae and other features of some amino acids

Name	Nature	Abbreviation	Structural Formula
Glycine	Neutral	Gly	$CH_2(NH_2)-COOH$
Alanine	Neutral	Ala	$CH_3-CH(NH_2)-COOH$
Valine	Neutral	Val	$CH_3-CH(CH_3)-CH(NH_2)-COOH$
Proline	Neutral	Pro	
Aspartic Acid	Acidic	Asp	$HOOC-CH_2-CH(NH_2)-COOH$
Glutamic acid	Acidic	Glu	$HOOC-CH_2-CH_2-CH(NH_2)-COOH$
Lysine	Basic	Lys	$CH_2(NH_2)-(CH_2)_3-CH(NH_2)-COOH$
Histidine	Basic	His	

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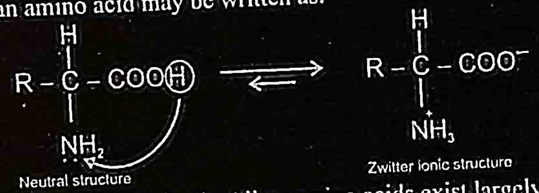
Structure of Amino Acids

Q14. What are zwitterions?

Zwitterion (Dipolar ion)

Definition: An ion that has positive and negative charges present within the molecule is called Zwitterion.

Formation: In the formation of Zwitterion, the proton (H^+) goes from the carboxyl group to amino group. The Zwitter ionic structure of an amino acid may be written as:



The dipolar structure is also called internal salt. All α–amino acids exist largely in dipolar ionic forms.

Acidic and Basic Characters of Amino Acids

On the basis of dipolar ion structure, the acidic and basic reactions of amino acids may be represented as:

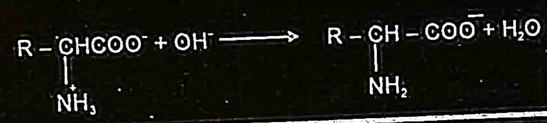
1. Basic character

When an acid is added to an amino acid, the carboxylate ion accepts the proton and, therefore, the basic character is due to this group.



2. Acidic character

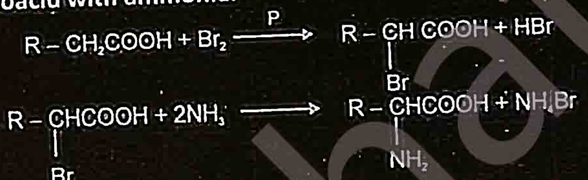
When an alkali is added to an amino acid, $-NH^+_3$ group releases the proton and therefore, the acidic character is due to this group.



Synthesis of Amino Acids

Amino acids can be synthesized by the following reactions.

1. By the reaction of α–bromoacid with ammonia.

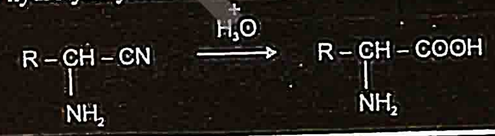


2. The Strecker Synthesis

When hydrogen cyanide is added to an aldehyde in the presence of ammonia, α–amino acid is obtained.



α–amino nitrile upon acidic hydrolysis yields an α–amino acids.



MCQ's

When acetaldehyde is treated with aqueous solution of HCN in ammonia, the amino acid formed is

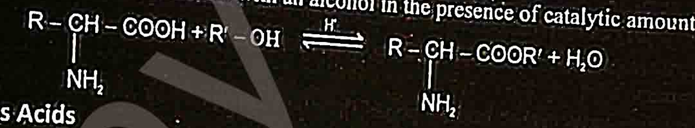
(a) Glycine (b) Alanine
(c) Valine (d) Lysine

Reaction of Amino Acids

Amino acids undergo many chemical reactions characteristics of either amino group or carboxyl group.

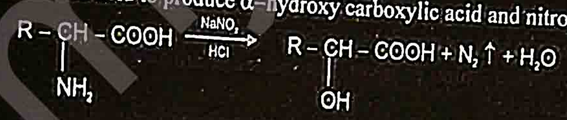
1. Esterification

Amino acids form aminoester when treated with an alcohol in the presence of catalytic amount of a strong acid.



(ii) Reaction with Nitrous Acids

Amino acids react with nitrous acid to produce α–hydroxy carboxylic acid and nitrogen gas.



Test of Amino Acids

Ninhydrin Test

Ninhydrin reacts with amino acid to form an intensely coloured bluish violet product. The ninhydrin reaction is also widely used to "visualize" amino acids separated by paper chromatography.

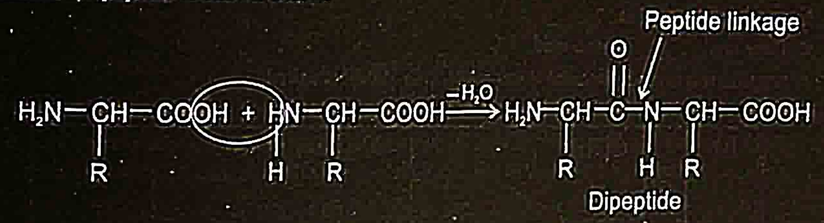
PEPTIDES

"The compounds formed by the condensation of two or more same or different α–amino acids with the elimination of water are called peptides."

Peptide linkage:

In this case, the carboxyl group of one amino acid and amino group of another amino acid gets condensed with elimination of water. The resulting –CO–NH– linkage is called a peptide linkage.

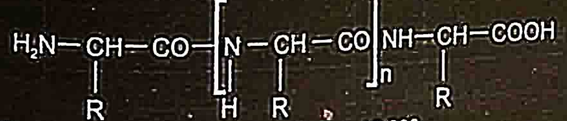
The formation of peptide is shown below:



Polypeptide:

If a large number of amino acids (hundreds to thousands) are joined by peptide bonds, the resulting polyamide is called a polypeptide.

Depending upon the number of amino acids per molecule, the peptides are dipeptides, tripeptides, polypeptides etc.



The molecular mass of polypeptides is upto 10,000

Peptide	Composition
Dipeptide	Which are made up of two amino acids.
Oligopeptide	Which are made up of two to nine amino acids.
Polypeptide	Having molecular mass up to 10,000
Proteins	Having molecular mass from 10,000 to 40000000.

Protein:

The formation of peptide bonds can continue until a molecule containing several hundred thousand amino acids is formed. Such a molecule is called polypeptide or protein.The molecular mass of protein is more than 10,000

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KEY TERMS

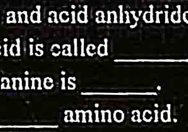
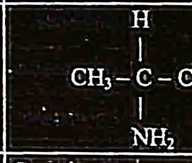
1. Organic compounds containing carboxyl group (– COOH) are called carboxylic acids. There are two classes of carboxylic acids i.e., aliphatic and aromatic carboxylic acids. Aliphatic carboxylic acids are also called fatty acids.
2. Carboxylic acids can be produced by the oxidation of alcohols and aldehydes and by hydrolysis of nitriles.
3. Lower members of the series are water soluble and have pungent smell. Solubility decreases with the increase in molecular mass.
4. Carboxylic acids have higher boiling points than the corresponding alcohols. Boiling point increases with the increase in the molar mass.
5. Acid chlorides, acid amides, esters and acid anhydrides are called derivative of carboxylic acids.
6. Acetic acid is synthesized on commercial scale from acetylene.
7. Carboxylic acids containing amino group in their molecules are called amino acids. They are classified as neutral, basic and acidic amino acids.
8. Amino acids join together to produce peptides. A polypeptide has a molecular mass up to 10,000 whereas the molecular mass of protein is greater than 10,000.

SOLVED OBJECTIVE EXERCISE

Q1. Fill in the blanks.

(i) Formula of malonic acid is _____.
(ii) Methyl nitrile upon acidic hydrolysis produces ____
(iii) Melting points of carboxylic acids containing even number of carbon atoms are _____ than the next lower and higher members containing odd number of carbon atoms.
(iv) Acetic acid on heating with _____ produces acetic anhydride.
(v) Acid chloride and acid anhydride are called _____ of acid.
(vi) Pure acetic acid is called _____.
(vii) Formula of alanine is _____.
(viii) Proline is a _____ amino acid.
(ix) A peptide having a molecular mass more than 10000 is called _____.

Answer Key.

(i)		(ii)	Acetic acid
(iii)	More	(iv)	P_2O_5
(v)	Derivatives	(vi)	Glacial acetic acid
(vii)		(viii)	Neutral
(ix)	Protein		

Q2. Indicate True or false.

(i) Acetic acid exists as a dimer in benzene.
(ii) First three aliphatic acids have fruity smells.
(iii) Carboxylic acids on reduction with $LiAlH_4$ produce alkenes.
(iv) Acetic acid on dehydration produces CO and H_2.
(v) Sodium formate on heating with soda lime produces $NaHCO_3$ and hydrogen.
(vi) Amino acids exist as Zwitter ion.
(vii) Histidine is an acidic amino acid.

(viii) A peptide having molecular mass upto 10000 is called protein.
(ix) Phthalic acid is a monocarboxylic acid.
(x) Formula of glycine is CH_2COOH.

Answer Key.

(i)	True	(ii)	False	(iii)	False	(iv)	False	(v)	False
(vi)	True	(vii)	False	(viii)	False	(ix)	False	(x)	False

Q3. Multiple choice questions. Encircle the correct answer.

(i) Acetic acid is manufactured by
(a) distillation (b) fermentation (c) ozonolysis (d) esterification

(ii) A carboxyl acid contains
(a) a hydroxyl group (b) a carboxyl group
(c) a hydroxyl and carboxyl group. (d) a carboxyl and an aldehydic group

(iii) Which acid is used in the manufacture of synthetic fiber
(a) formic acid (b) oxalic acid (c) carbonic acid (d) Acetic acid

(iv) Which of the following derivative can not be prepared directly from acetic acid.
(a) acetamide (b) acetyl chloride (c) acetic anyhdirde (d) ethyl acetate

(v) Which reagent is used to reduce a carboxylic group to an alcohol.
(a) H_2 / Ni (b) H_2 / Pt (c) $NaBH_4$ (d) $LiAlH_4$

(vi) The solution of which acid is used for seasoning of food.
(a) Formic acid (b) Acetic acid (c) Benzoic acid (d) Butanoic acid

(vii) Organic compounds X and Y react together to from organic compound Z. What type of Compounds can Z, Y and Z be?

	X	Y	Z		X	Y	Z
(a)	alcohol	ester	acid	(b)	acid	ester	alcohol
(c)	ester	alcohol	acid	(d)	alcohol	acid	ester

(viii) An aqueous solution of an organic compound reacts with sodium carbonate to produce carbon dioxide gas. Which one of the following could be the organic compound.
(a) CH_2=CH-CH_3 (b) CH_3-CHO (c) $CH_3COOC_2H_5$ (d) CH_3-CH_2-COOH

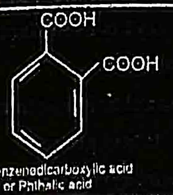
(ix) Which of the following is not a fatty acid?
(a) Propanoic acid (b) Acetic acid (c) Phthalic acid (d) Butanoic acid

(x) Acetamide is prepared by
(a) Heating ammonium acetate (b) Heating methyl cyanide
(c) Heating ethyl acetate (d) The hydrolysis of methyl cyanide

Solved Exercise MCQs

Q.No	Answer	Reason
(i)	(b) Fermentation	Fermentation yields alcohol which gives acetic acid by strongly oxidation.
(ii)	(b) a carboxyl group	R – COOH, Here – COOH is carboxyl group.
(iii)	(d) Acetic acid	Acetic acid forms silk which is synthetic fibre.
(iv)	(a) Acetamide	CH_3COOH reacts with NH_3 to form ammonium acetate which gives acetamide on heating.

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(v)	(d) $LiAlH_4$	$CH_3-\overset{O}{\overset{\|}{C}}-OH + 4[H] \xrightarrow{LiAlH_4} CH_3-CH_2-OH + H_2O$
(vi)	(b) Acetic acid	5% CH_3COOH is vinegar used in seasoning of food.
(vii)	(d) X = alcohol Y = Acid Z = Ester	$CH_3COOH + C_2H_5OH \rightleftharpoons[H_2SO_4] CH_3COOC_2H_5 + H_2O$
(viii)	(d) CH_3CH_2COOH	Carboxylic acid + Carbonates → Salt + CO_2 + H_2O
(ix)	(c) Phthalic acid	 Phthalic acid is aromatic acid. 1,2-Benzenedicarboxylic acid or Phthalic acid
(x)	(a) Heating ammonium acetate	$CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 + H_2O$

SOLVED ANSWERS TO EXERCISE

Q4. Write down the structural formulae of the followings

(i) Valeric acid (ii) Propionic acid (iii) Oxalic acid

(iv) Benzoic acid (v) Acetic anhydride (vi) Acetyl chloride

Ans. Structural Formulas.

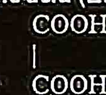
(i) Valeric acid (Pentanoic acid):

$CH_3-CH_2-CH_2-CH_2-COOH$

(ii) Propionic acid (Propanoic acid):

CH_3-CH_2-COOH

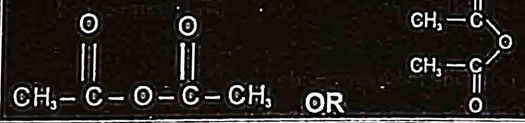
(iii) Oxalic acid (Ethanedioic acid):



(iv) Benzoic aicd:



(v) Acetic anhydride:



(vi) Acetyl chloride:



Q5. Write down the names of the following compounds by IUPAC system.

Ans. IUPAC names:-

(i)

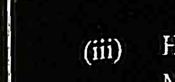


Propanedioic Acid

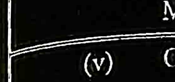
(ii)



1, 3-Benzenedioic acid

(iii)  Methanoic acid

(iv)  Ethyl ethanoate

(v)  2-Aminoethanoic acid

(vi) $HCOOC_3H_7$ Propyl methanoate

Q6. (b) How would you convert acetic acid into the following compounds?

(i) Methane (ii) Acetyl chloride (iii) Acetamide (iv) Acetic anhydride

Ans. (b) Conversions

(i) Acetic acid into Methane

- $CH_3COOH + NaOH \longrightarrow CH_3COO^-Na^+ + H_2O$
- $CH_3COO^-Na^+ + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$

(ii) Acetic acid into Acetylchloride:

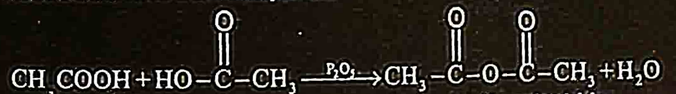
$$CH_3COOH + SOCl_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-Cl + SO_2 + HCl$$

(iii) Acetic acid into Acetamide:

$CH_3COOH + NH_3 \longrightarrow CH_3COO^-NH_4^+$

$CH_3COO^-NH_4^+ \xrightarrow{Heat} CH_3CONH_2 + H_2O$

(iv) Acetic acid into acid anhydride



Acetic anhydride

Q7.(b) What is vinegar? Describe how is vinegar prepared from ethanol?

Ans. (b) Vinegar:

"Dilute (5 %) solution of acetic acid in water is called vinegar".

- It is a colourless liquid with a pungent smell and sour taste.

Preparation of Vinegar from Ethanol

When ethyl alcohol (C_2H_5OH) reacts with oxidizing agent like acidified potassium dichromate it converts into acetic acid.

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- $CH_3CH_2OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{O}{\overset{\|}{C}}-H + H_2O$
- $CH_3-\overset{O}{\overset{\|}{C}}-H + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{O}{\overset{\|}{C}}-OH$

Q8. How would you carry out the following conversions?
(i) Acetic acid into acetamide (ii) Acetic acid into acetone

Ans. **(i) Acetic acid into acetamide :**

$$CH_3COOH + NH_3 \longrightarrow CH_3COO^-NH_4^+$$

$$CH_3COO^-NH_4^+ \xrightarrow{\Delta} CH_3CONH_2 + H_2O$$

(ii) Acetic acid into acetone:

$$2CH_3COOH + Ca(OH)_2 \rightarrow (CH_3COO)_2Ca + 2H_2O$$

$$(CH_3COO)_2Ca \xrightarrow{Heat} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CaCO_3$$

Acetone

Q10. What happens when the following compounds are heated.
(i) Calcium acetate (ii) Sodium formate and soda lime (iii) Ammonium acetate

Ans. **Effect of heating on following:**

(i) Calcium acetate

$$(CH_3COO)_2Ca \xrightarrow{Heat} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CaCO_3$$

Acetone

(ii) Sod. formate and soda lime

$$HCOONa + NaOH \xrightarrow[\Delta]{CaO} H_2\uparrow + Na_2CO_3$$

(iii) Ammonium Acetate

$$CH_3COO^-NH_4^+ \xrightarrow{Heat} CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O$$

Q13. What is peptide bond? Write the formula of a dipeptide.

Ans. **Peptide bond:-**

A bond formed between carbon and nitrogen atom in a peptide or polyamide is called peptide bond.

In the reactions between amino acids, the carboxyl group of one amino acid and amino group of another amino acid get condensed with elimination of H_2O. The resulting (–CO–NH–) linkage is called as peptide linkage or peptide bond.

Example:

$$H_2N-\underset{R}{CH}-COOH + H_2N-\underset{H\ \ R}{CH}-COOH \xrightarrow{-H_2O} H_2N-\underset{R}{CH}-\overset{O}{\overset{\|}{C}}-\underset{H\ \ R}{N}-CH-COOH$$

Peptide linkage

Dipeptide

Formula of Dipeptide:

$$H_2N-\underset{R}{CH}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\underset{R}{CH}-COOH$$

Q16. Study the facts given in (a), (b) and (c) below and then answer questions which follow.

(a) A is an organic compound made up of C,H and O. It has a vapour density 15. [Hint: Molecular mass = 2 x Vapour density]

Ans. **(a) Molecular mass of organic compound (A)**

Molecular mass = 2 × Vapour density

= 2 × 15 = 30 amu

(b) On reduction A gives a compound X Which has the following properties.

(i) X is a colourless liquid miscible with water.

(ii) X is a neutral to litmus.

(iii) When X is warmed with a few drops of conc. H_2SO_4 followed by a little salicylic acid, a characteristic smell is produced.

Ans. **(b) Name of organic compound (A)**

The organic compound contains C, H and O, its molecular mass is 30 amu. The molecular mass shows that it is aldehyde not ketone or alcohol. The reason is that the smallest ketone is acetone having molecular mass 58 amu.

The simplest aldehyde which has molecular mass 30 amu is formaldehyde. Thus compound (A) is formaldehyde.

$$A = H-\overset{O}{\overset{\|}{C}}-H \text{ (Formaldehyde)}$$

Reduction of Compound (A)

$$H-\overset{O}{\overset{\|}{C}}-H + H_2 \xrightarrow{Pt} H-\underset{H}{\overset{H}{C}}-OH\ (X)$$

The reduction of compound (A) gives compound (X) having formula (CH_3-OH).

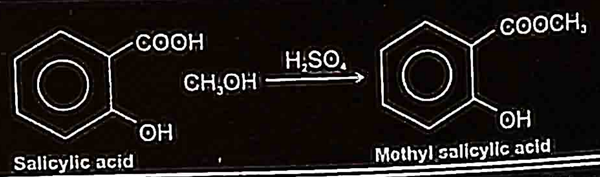
Properties of X (CH_3OH)

(i) Methyl alcohol CH_3OH is a colourless liquid miscible with water.

(ii) Methyl alcohol CH_3OH is a neutral to litmus.

(iii) When methylalcohol (CH_3OH) is warmed with few drops of Conc. H_2SO_4 and salicylic acid ($C_6H_4COOHOH$) a characteristic smell of methyl saliclic acid ($C_6H_4COOCH_3OH$) is obtained.

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Salicylic acid — Mothyl salicylic acid

(c) When X is subjected to strong oxidation, it gives compound B, which has the following properties.

(i) B is pungent smelling mobile liquid.
(ii) It is miscible with water, alcohol or ether.
(iii) It is corrosive and produces blisters on contact with skin.
(iv) B can be obtained by passing the vapours of A with air over platinum black catalyst.
(v) B liberates H_2 with sodium.
(vi) It gives CO_2 with $NaHCO_3$.

1. What is the molecular mass of A?
2. Identify A, X and B.
3. Give five appropriate reactions to confirm the identities of A, X and B.
4. State one large – scale use of either A, X or B.

Ans: **(c) Oxidation of compound (X)**

When Methylalcohol (CH_3OH), compound X, is treated with strong oxidizing agent it gives formic acid (B)

- $CH_3OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} H-\overset{O}{\overset{\|}{C}}-H + H_2O$
- $H-\overset{O}{\overset{\|}{C}}-H + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} H-\overset{O}{\overset{\|}{C}}-OH$

Properties of Formic acid (B)

(i) Formic acid (HCOOH) is a pungent smelling mobile liquid
(ii) It is miscible with water, alcohol and ether due to hydrogen bonding.
(iii) Formic acid is corrosive and produces blisters when contact with skin.
(iv) Formic acid can be obtained by passing the vapours of formaldehyde (A) with air over platinum black catalyst.

- $H-\overset{O}{\overset{\|}{C}}-H + \frac{1}{2}O_2 \xrightarrow{Pt-Black} H-\overset{O}{\overset{\|}{C}}-OH$

(A) (B)

(v) Formic acid (B) librates H_2 when reacts with Na
$2HCOOH + 2Na \rightarrow \underset{\text{Sodiumformate}}{HCOONa} + H_2$

(vi) Formic a id (B) gives CO_2 with $NaHCO_3$
$HCOOH + NaHCO_3 \rightarrow HCOONa + CO_2 + H_2O$

Result:
A = Formaldehyde (HCOH)
B = Formic acid (HCOOH)
X = Methylalcohol (CH_3OH)

Previous Board Questions

1. Write four uses of Acetic Acid.
2. Write down the structural formulas of:
   (a) Isobutyric Acid (b) Oxalic Acid
3. What are essential and non-essential amino acids?
4. What are acidic amino acids? Give one example.
5. How the Hydrolysis of Esters gives carboxylic acid?
6. How the Carboxylic acid can be converted into α – amino acids?
7. Write structural formulas of :
   (a) Lactic acid (b) Iso-butyric acid
8. What are zwitterions? Write equation.
9. What is a peptide bond? Write the formula of a dipeptide.
10. How ethanol is converted into acetic acid and vice versa.
11. The molecular mass of carboxylic acids becomes double in non-polar solvent.
12. Write down the structure formula of
    (a) Valeric acid (b) Histidine
13. What are fatty acids? Give an example.
14. Define proteins. How do these differ from polypeptides?
15. How will you convert
    (a) Acetic acid into acetamide (b) Acetic acid into acetone
16. How do the following reagents react together? Give reactions with conditions
    (a) $CH_3COOH + HI$ (b) $CH_3COOH + Li\,A\ell H_4$
17. How acetic acid is prepared on the commercial scale from acetylene?
18. What are basic amino acids? Give two examples.
19. What is Strecker synthesis?

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- Additional Board Short Answers Questions
- Past Board Papers

CHAPTER 14

MACROMOLECULES

INTRODUCTION:

Acceptance of the macromolecular hypothesis came about in 1920's largely because of the efforts of Staudinger. He proposed long chain formulas for polystyrene, rubber and polyoxymethylene.

Macromolecules

"Macromolecules or polymers are large molecules built up from small repeating units called monomers."

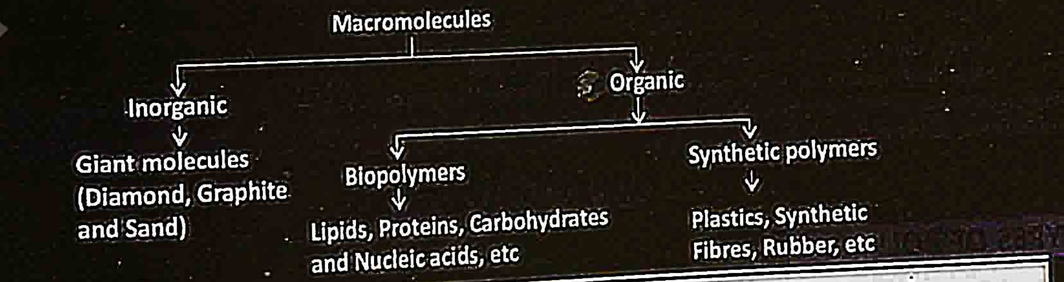
- The development of the process of polymerization is, perhaps, one of the most significant things chemists have done, where it has had the major effect on everyday life.
- The world would be a totally different place without artificial fibres, plastics, etc.
- One of the most significant changes has been the gradual replacement of natural materials such as wood and cotton with man-made synthetic polymers.
- All polymers are macromolecules but all macromolecules are not polymers.

For better or worse we are living in a "plastic" society.

MCQ's
Which of the following is not a polymer?
(a) DNA (b) Nylon-6,6
(c) Graphite (d) Dacron

Classification of Macromolecules

Macromolecules can be classified into the following types.



POLYMERS

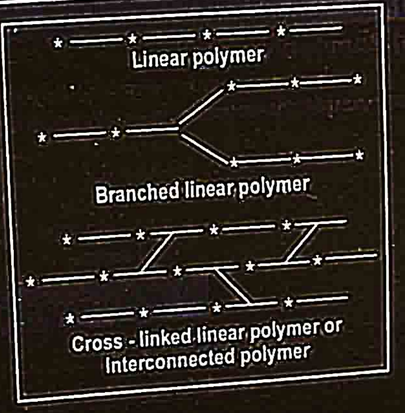
"A large size molecule build up by the repetition of small and simple chemical units (monomers) is called polymer."

$$n(\text{Monomer}) \xrightarrow{\text{Polymerization}} (\text{monomer})_n$$

$\downarrow$

Polymer

- The word polymer is derived from Greek, poly means 'many' and 'mer' means 'parts'.
- For a compound to occur as monomer, it must have two reactive sides or bifunctional.
- The bond in each polymer is covalent.



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STRUCTURE OF POLYMERS

On the basis of structure, polymers are of three types:

(i) Linear polymers

These are the polymers in which the monomers are joined together to form long straight chains. e.g. Polythene, PVC, polyesters and nylons, etc.

(ii) Branched chain polymers

In these polymers, the monomeric units are joined to produce long chains (called the main chain) along with side-chains of different lengths which produce branches. e.g. Amylopectin, glycogen, etc.

(iii) Cross-linked polymers

In these polymers, the initially formed linear polymer chains are joined together to form a **three dimensional** network structure. e.g. Bakelite, urea-formaldehyde etc.

Q. What is D.P? How can you calculate the molecular mass of a polymer from its DP?

Ans.

Degree of polymerization (D.P)

"The number of repeating units which determine the length of the polymer chain is called degree of polymerization".

Calculation of molecular mass:

The molecular mass of a polymer is the product of molecular mass of the repeating unit and the DP.

Example:

Vinyl chloride polymerizes to give polyvinyl chloride (PVC).

$$n\,CH_2=CH \longrightarrow -CH_2-\underset{Cl}{CH}-CH_2\Big)_{n-1}\underset{Cl}{CH}-$$

Vinyl chloride — Polyvinyl chloride (PVC)

Where the DP of polyvinyl chloride is 1000 and molecular mass its repeating unit is 63.

Molecular mass of PVC = Molecular mass of repeating unit × DP

= 63 × 1000

= 63000

Hence, the molecular mass of polyvinyl chloride is 63000.

Most high molecular mass polymers are useful for making plastics, rubbers or fibres, etc. and have molecular masses between 10,000 to 1,000,000. The properties of polymeric materials vary widely depending upon the chemical composition and structure of the macromolecule.

TYPES OF POLYMERS

The polymers may be classified in a number of ways as:

(i) On the basis of nature of monomers (ii) On the basis of heating effect (iii) On the basis of synthesis

(i) On the basis of nature of monomers

(a) Homopolymer:

A homopolymer is formed by the polymerization of a single type of monomer.

For example, the polymerization of vinyl acetate.

$$n\,CH_2=\underset{OCOCH_3}{CH} \longrightarrow \left[CH_2-\underset{OCOCH_3}{CH}-CH_2-\underset{OCOCH_3}{CH}-CH_2-\underset{OCOCH_3}{CH}-\right]_n$$

Vinyl acetate — Homopolymer (Polyvinyl acetate)

Homopolymer	Monomer
1. Polyethylene	$H_2C=CH_2$ (Ethylene)
2. Polyvinyl chloride (PVC)	$H_2C=CHCl$ (Vinyl chloride)

3. Polystyrene	$C_6H_5CH=CH_2$ (Styrene)
4. Polyacrylonitrile (PAN) or Orlon	$H_2C=CH-CN$ (Acrylonitrile)
5. Teflon (Polytetrafluoroethene)	$F_2C=CF_2$ (Tetrafluoroethylene)

(ii) Copolymer:

A copolymer is formed by the polymerization of two different monomers together.

For example: Vinyl acetate reacts with butyl maleate to give a copolymer.

$$n\,CH_2=\underset{OCOCH_3}{CH} + n\,\underset{COOBu}{CH}=\underset{COOBu}{CH} \longrightarrow \left[CH_2-\underset{OCOCH_3}{CH}-\underset{COOBu}{CH}-\underset{COOBu}{CH}-CH_2-\underset{OCOCH_3}{CH}\right]_n$$

Vinyl acetate — Butyl maleate — Copolymer

Co-Polymer	Monomers
1. Dacron or Terylene	(i) $HOCH_2-CH_2OH$ (Ethylene glycol) (ii) $H_3COOC(C_6H_4)COOCH_3$ (Dimethyl terephthalate)
2. Glyptal	(i) $HOCH_2-CH_2OH$ (Ethylene glycol) (ii) $HOOC(C_6H_4)COOH$ (Phthalic acid)
3. Nylon -6,6	(i) $H_2N(CH_2)_6NH_2$ (Hexamethylene diamine) (ii) $HOOC(CH_2)_4COOH$ (Adipic acid)
4. Bakelite	(i) HCHO (Formaldehyde) (ii) C_6H_5OH (Phenol)

(iii) Terpolymer:

In terpolymer, three different monomers are polymerized and the polymerization reaction is carefully controlled.

For example: Combination of butyl acrylate, methacrylate and acrylic acid monomers gives a highly tough polymer which serves as a weather-resistant paint.

(ii) On the basis of heating effect

Thermoplastic Polymers	Thermosetting polymers
• "A polymer which becomes softened repeatedly on heating and hardened when cooled with a little change in properties is called thermoplastic polymer".	• "A polymer which becomes hard on heating and cannot be softened again is called thermosetting polymer".
• They can be remoulded, recast and reshaped.	• They cannot be remoulded or reshaped.
• Weak intermolecular forces are present which become weak on heating.	• Strong intra molecular forces are present that is why thermosetting polymer, on heating, decomposes instead of melting.
• They are less brittle and soluble in some organic solvents.	• They are more brittle and insoluble in organic solvents.
• They are formed by addition polymerization.	• They are formed by condensation polymerization.
• They have usually linear structures.	• They have three dimensional cross-linked structures.
Examples: Polythylene, PVC, Teflon, etc.	**Examples :** Bakelite, Ureaformaldehyde, Resin, Terylene, etc.

(iii) On the basis of synthesis

On the basis of synthesis the polymers can be classified into two classes:

(i) addition polymers (ii) condensation polymers

This can be explained by their way of polymerization.

Polymerization Process

In 1929, W.H. Carothers suggested a classification of the polymerization process into two types depending upon the way the polymers are formed.

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1. Addition polymerization or chain growth polymerization
2. Condensation polymerization or step growth polymerization

Q19. Differentiate between addition and condensation polymerization.

	Addition Polymerization		Condensation Polymerization
	"The polymerization in which unsaturated monomers combine to form a product (polymer) without the elimination of small molecule is called addition polymerization".		"The polymerization in which monomers having functional group combine to give a product (polymer) with the elimination of small molecule (e.g H_2O/CH_3OH) is called condensation polymerization".
o	It involves free-radical mechanism.	o	It does not involve free-radical mechanism whether it is ionic in nature.
o	It completes in three steps i.e. Initiation propagation and termination.	o	It completes in a single step.
o	The length of the chain increases only from one side. **Example:** Polymerization of styrene. $n\,CH_2=CH(C_6H_5) \longrightarrow -CH_2-(CH(C_6H_5)-CH_2)_{n-1}-CH(C_6H_5)-$ Styrene → Polystyrene	o	The length of chain increases from both ends/ sides. **Example:** Terephthalic acid and ethylene glycol are condensed to give Dacron. $n\{HO-C_6H_4(COOH)-OH + HO-CH_2-CH_2-OH\} \longrightarrow [-OC-C_6H_4-COO-CH_2-CH_2-O-]_n + 2nH_2O$ Terephthalic acid + Ethylene glycol → Dacron (polyester)

Addition polymerization (free radical mechanism)

Initiation:

$$R-C(=O)-O-O-C(=O)-R \xrightarrow{\Delta} 2R-C(=O)-O\cdot$$

Organic peroxide

$$2R-C(=O)-O\cdot \longrightarrow 2R\cdot + 2CO_2$$

Propagation:

$$R\cdot + CH_2=CH(C_6H_5) \longrightarrow R-CH_2-\dot{C}H(C_6H_5)$$

$$R-CH_2-\dot{C}H(C_6H_5) + CH_2=CH(C_6H_5) \longrightarrow RCH_2-CH(C_6H_5)-CH_2-\dot{C}H(C_6H_5)$$

Termination:

$$R-(CH_2-\dot{C}H(C_6H_5))_n + R\cdot \longrightarrow R-(CH_2-CH(C_6H_5))_n-R$$

BRIEF DESCRIPTION OF SYNTHETIC POLYMERS

1. Polyvinyl Chloride (PVC)

It is an addition polymer obtained by polymerizing vinyl chloride at 52°C at 9 atmospheric pressure.

$$n\,CH_2=CH(Cl) \xrightarrow[52^\circ C]{9\ atm} -CH_2-(CH(Cl)-CH_2)_{n-1}-CH(Cl)-$$

Vinyl chloride → Polyvinyl chloride (PVC)

- Addition of plasticizer improves the flexibility of the polymer.

Uses:

It is widely used in:
(i) floor coverings (ii) pipes (iii) gramophone recorders, etc.

Substances, which are sometimes added to plastics to impart viscosity, flexibility, softness or other properties to finished produces, are called plasticizers/usually esters of phthalic acid.
E.g dimethyl phthalic is added to soften the hard PVC.

2. Polystyrene

It is also an addition polymer and is obtained by the polymerization of styrene in the presence of a catalyst.

$$n\,CH_2=CH(C_6H_5) \longrightarrow -CH_2-(CH(C_6H_5)-CH_2)_{n-1}-CH(C_6H_5)-$$

Styrene → Polystyrene

Uses:

Polystyrene is used in the manufacture of:
(i) food containers (ii) cosmetic bottles (iii) toys (iv) packing materials, etc.

3. Polyvinyl Acetate (PVA)

It is an addition polymer and is obtained by polymerization of vinyl acetate.

$$n\,CH_2=CH(OCOCH_3) \longrightarrow [CH_2-CH(OCOCH_3)-CH_2-CH(OCOCH_3)]_n$$

PVA

- PVA is a colourless, non-toxic resin.
- The resin has a characteristics odour.

Q. What are acrylic resins and give their uses?

Uses:

It is mostly used as:
(i) an adhesive material (ii) a binder for emulsion paints.

4. Acrylic Resins

Acrylic resins are closely related to vinyl resins. The most important monomers of acrylic resins are:

$CH_2=CHCOOH$ (Acrylic acid) $\quad CH_2=C(COOCH_3)-CH_3$ (Methylmethacrylate) $\quad CH_2=CH-CN$ (Acrylonitrile)

Uses:-

It is used in the manufacturing of:
(i) plastics (ii) paints for car industry (iii) water based weather resistant paints

5. Polyester Resins

Polyester resins are the product of the reaction of an alcohol (ethane 1, 2 diol) and aromatic bi-functional acids (benzene 1, 4 dicarboxyoic acid).

$$n\{HO-C_6H_4(COOH)-OH + HO-CH_2-CH_2-OH\} \longrightarrow [-OC-C_6H_4-COO-CH_2-CH_2-O-]_n + 2nH_2O$$

Terephthalic acid + Ethylene glycol → Dacron (polyester)

Uses:

This product has a large number of uses in:

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(i) clothing
(ii) polyester is often blended with cotton or wool for summer and winter clothing
(iii) polyester resins are also used for making water tanks, etc.

6. Polyamide Resins

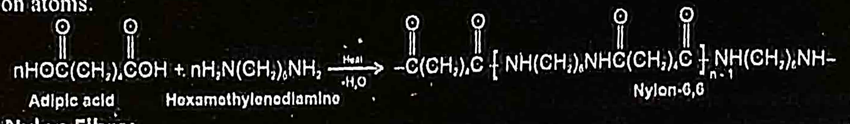
These resins are formed by the condensation of polyamines with aliphatic dicarboxylic acids. One of the most famous condensation polymers discovered is Nylon. The word Nylon has been accepted as a generic name for synthetic polyamides.

Nylon - 6, 6

- Nylon -6,6 is the most important polyamide.
- It is obtained by heating adipic acid (hexanedioic acid) with hexamethylene diamine.

Why Nylon 6, 6:

Because nylon6,6 derives its name from its starting materials adipic acid and hexamethylene diamine, both of which have six carbon atoms.



Characteristics of Nylon Fibre:

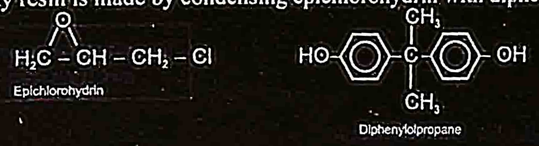
It has high strength, elasticity, toughness and abrasion resistance.

Use:

Nylon is mainly used as a textile fibre.

7. Epoxy Resins

- The epoxy resins are fundamentally polyethers but retain their name on the basis of their starting materials and the presence of epoxide group in the polymer.
- The epoxy resin is made by condensing epichlorohydrin with diphenylol propane:



Uses:

(i) The major use of epoxy resins is in coating materials which give toughness, flexibility, adhesion and chemical resistance.
(ii) Industrial materials, thermal power stations, packing materials are coated with epoxy paints.
(iii) Dams, bridges, floors etc. are painted with epoxy resins.

Q5. Write notes on: (a) Polyester resins (b) Polyamide resins (c) Epoxy Resins

BIOPOLYMERS

Most biologically important substances are organic compounds built up from skeleton of carbon atoms. Many of them are very large molecules and most of these are polymers. The four major classes of organic compounds in living cells are carbohydrates, lipids, proteins and nucleic acids.

Q7. What are carbohydrates and how are they classified?

CARBOHYDRATES

Definition

"The polyhydroxy compounds of aldehydes and ketones are called carbohydrates."

The term carbohydrate is applied to a large number of relatively heterogeneous compounds. They are the most abundant biomolecules on earth. The name carbohydrate (hydrate of carbon) is derived from the fact that the first compound of this group which was studied had an empirical formula $C_x(H_2O)_y$. Usually they have H:O same as in water (2:1).

Classification of Carbohydrates

The commonly described classification is given below.

Carbohydrates

Sugars
- Crystalline solids
- Soluble in water
- Sweet in taste
- Micromolecules

Non - sugars
- Amorphous solids
- Insoluble in water
- Tasteless
- Macromolecules

Monosaccharides
- Simplest suger
- Cannot be hydrolize
- Aldoses or Ketoses
- e.g. Glucose, fructose etc.

Oligosaccharides
- Contain 2 - 9 monosaccharides
- can be hydrolize
- di, tri, tetra saccharides
- e.g. sucrose, lactose etc.

Polysaccharides
- Contain more than 9 monosaccharides
- can be hydrolize
- Have structural and storage function
- e.g. Starch, Cellulose, Glycogen etc.

1. Monosaccharides

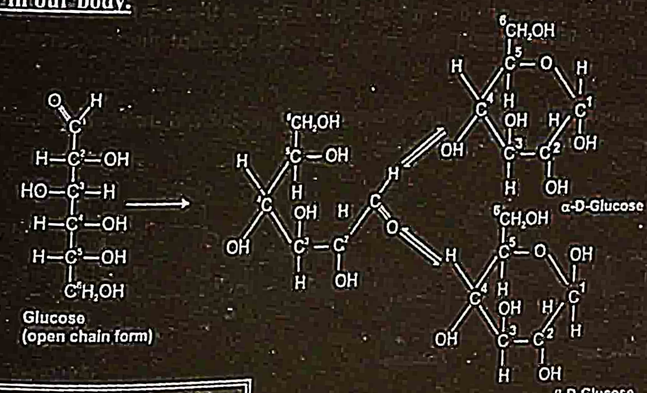
- These are simple sugars which cannot be hydrolyzed.
- They have an empirical formula $(CH_2O)_n$ where n = 3 or some large number.
- There are 20 monosaccharides which occur in nature.

Classification of Monosaccharides

Based on number of Carbon Atoms		Based on Functional Group
3 C	Trioses	Having aldehydic group = Aldoses Aldotriose = Glyceraldehyde Aldopentoses = Ribose, Xylose Aldohexoses = Glucose, Mannose, Galactose
4 C	Tetroses	
5 C	Pentoses	
6 C	Hexoses	
7 C	Heptoses	Having ketonic group = Ketoses Ketotriose = Dihydroxy acetone Ketopentose = Ribulose Ketohexoses = Fructose, Sorbose
8 C	Octoses	
9 C	Nonoses	

Glucose

Glucose also called:
(i) **Dextrose** because it occurs in nature as the optically active dextrorotatory isomer.
(ii) **Grape sugar** because it is present in most sweet fruits specially grapes and in honey.
(iii) **Blood sugar** because small quantities of glucose are also present in human blood and urine. The blood normally contains 65 to 110 mg of glucose per 100 mL.
In the combined state, it forms a major component of many disaccharides and polysaccharides.
It is the source of energy in our body.

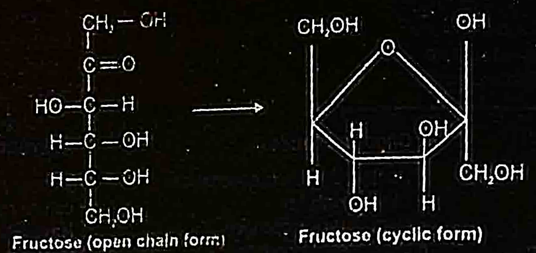


α-D-Glucose 36% ⇌ Open chain form 0.02% ⇌ β-D-Glucose 64%

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Fructose

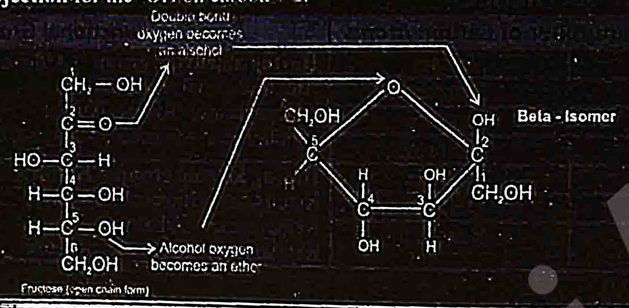
- Fructose is also found in combined and free states.
- It is used as a sweetening agent in confectionery.
- It is used as a substitute of cane sugar.



Compare Alpha and Beta Fructose

The Beta position is defined as the -OH being on the same side of the ring as the C # 6. In the ring structure this results in a upwards projection for the -OH on carbon # 2.

The Alpha position is defined as the -OH being on the opposite side of the ring as the C # 6. In the ring structure this results in a downward projection for the -OH on carbon # 2.



2. Oligosaccharides

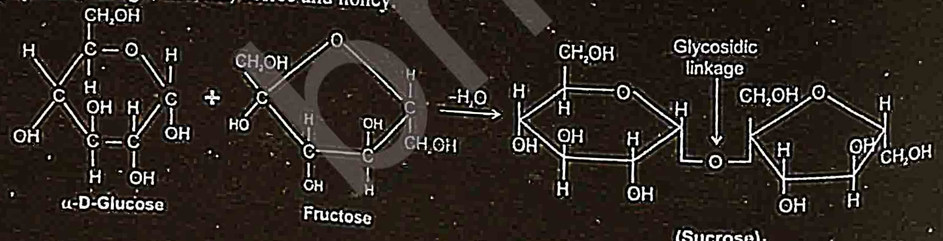
"The carbohydrates which are formed when two to nine monosaccharide units combine by glycosidic linkage by the loss of water molecules are called oligosaccharides."

or

"The carbohydrates which upon hydrolysis by water in the presence of an acid or by enzymes yield two or more monosaccharides units are called oligosaccharides."

Examples:

(i) Sucrose: It is a common table sugar and is a disaccharide of glucose and fructose. It occurs in sugar cane, sugar beet, pineapple, apricot, mango, almond, coffee and honey.



(ii) Lactose (milk sugar): It is a disaccharide of glucose and galactose. It occurs in the milk of all animals. It does not occur in plants.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Galactose}}{C_6H_{12}O_6}$$
Lactose

(iii) Maltose: It is a disaccharide of two glucose molecules.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{(Enzyme maltase)}]{H^+} 2C_6H_{12}O_6$$
Maltose — Glucose.

Maltose	$\xrightarrow{H_2O}$ Glucose + Glucose
Lactose	$\xrightarrow{H_2O}$ Glucose + Galactose
Sucrose	$\xrightarrow{H_2O}$ Glucose + Fructose

(iv) Raffinose: It is a Trisaccharide which yields three monosaccharide molecules on hydrolysis. It has molecular formula, $C_{18}H_{32}O_{16}$.

$$C_{18}H_{32}O_{16} + 2H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} + \underset{\text{Galactose}}{C_6H_{12}O_6}$$
Raffinose

Reducing sugar	Non-reducing sugars
D-Glucose, *D*-Fructose	Sucrose, Starch
Maltose, Lactose	Glycogen, Cellulose

3. Polysaccharides

"The carbohydrates of high molecular mass which yield many monosaccharide molecules on hydrolysis are called polysaccharides."

- The general formula of polysaccharides is $(C_6H_{10}O_5)_n$. e.g. starch, cellulose, glycogen etc.
- The polysaccharides are:

(i) amorphous solids (ii) insoluble in water (iii) tasteless (iv) 'non-sugars

Principal Functions

(i) They are used as energy storage compounds (starch in plants and glycogen in animals and is stored in the liver and muscles).

(ii) They are used for building structural elements of cells (cellulose is used to form cell walls and other structural features of the plants).

(a) Starch $(C_6H_{10}O_5)$

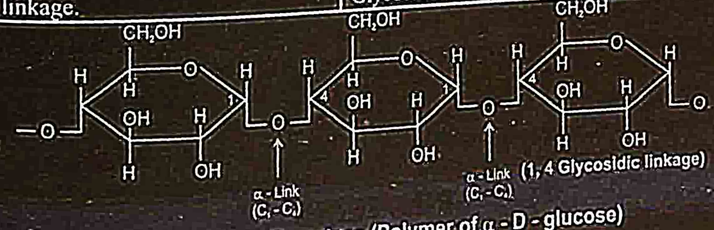
It is a white amorphous substance with no taste and smell. It is the most important source of carbohydrates in human diet. The chief commercial sources of starch are wheat, rice, maize, potatoes and barley.

Starch is a polymer of **α-D-glucose.** Starch is not a pure compound. It is a mixture of two polysaccharides, amylose and amylopectin which can be separated from one another.

13. Differentiate between Amylose and Amylopectin?

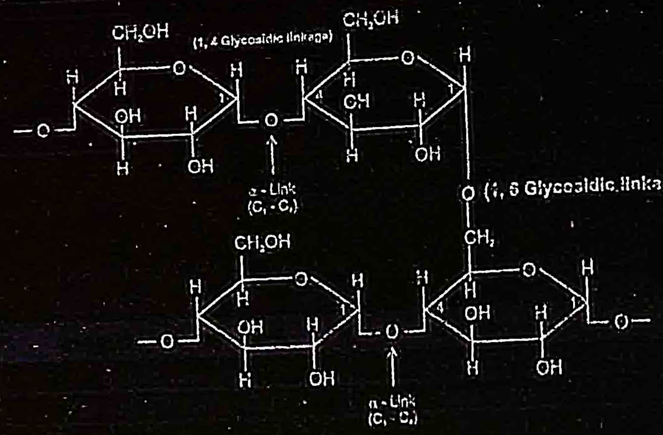
Ans:

Amylose	Amylopectin
It is soluble in water.	It is insoluble in water.
It gives deep blue colour with Iodine.	It gives no colour with Iodine.
Natural starch consists of 10-20% amylose.	Natural starch consists of 80-90% amylopectin.
It is a linear polymer.	It is a highly branched polymer.
It is a polymer of ∝-D-Glucose having 1, 4 Glycosidic linkage.	It is a polymer of ∝-D-Glucose having 1, 4 and 1, 6 Glycosidic linkages.



Structure of amylose (Polymer of α - D - glucose)

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Structure of amylopectin (Polymer of α - D - glucose)

Uses of starch:

(i) It is used in coating and sizing of paper to improve the writing qualities.
(ii) It is also used in laundering.
(iii) It is used in the manufacture of glucose and ethyl alcohol.

(b) Cellulose

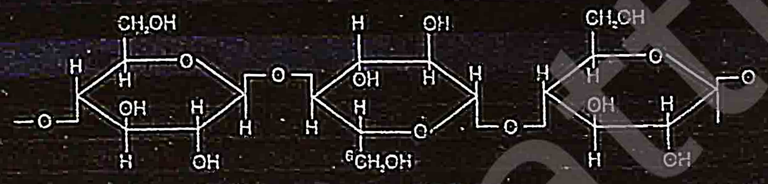
The most abundant structural polysaccharide is cellulose.

Occurrence:

- Some 100 billion tons of cellulose are produced each year by plants. For example, cotton is 99% celluiose and the woody parts of trees are generally more than 50% cellulose.
- It is present mainly in the plant kingdom but also occurs in some marine animals.

Structure:

It is a polymer of β-D-glucose. It is an unbranched polymer consisting of large number (up to 2500) of glucose residues joined to each other through β-1→4 linkages.



Cellulose (Polymer of β-D-Glucose)

(c) Glycogen

Occurrence:

It occurs mainly in the liver and muscles. Animals store glucose in the form of glycogen. Glycogen is also called 'animal starch'.

Structure:

Its structure closely resembles with that of amylopectin having 1→4 and 1→6 glycosidic linkages. Human glycogen is much more branched molecule than amylopectin. On hydrolysis it yields glucose units.

PROTEINS

"The extremely complicated high molecular weight organic material, which upon complete hydrolysis, yield amino acids, are called proteins."

Meaning: The name protein is derived from the Greek word proteios-meaning "prime importance".

Proteins are the nitrogeneous compounds made up of variable number of amino acids. The human body probably contains at least 10,000 different kinds of proteins.

Proteins are present in all living organisms and without proteins life would not be possible. They are present in muscles, skin, hair and other tissues that make up the bulk of the body's non-bony structure.

Elements of Proteins:

- **Major elements** present in proteins are carbon, hydrogen, oxygen, nitrogen, and phosphorus.
- **Trace elements** which are present in protein are iron, copper, iodine, manganese, sulphur and zinc.

Classification of Proteins

(a) Based on the physico – chemical properties

Based on the physico – chemical properties, proteins may be classified into three types.

1. Simple proteins 2. Compound or conjugated proteins 3. Derived proteins

1. Simple proteins

These proteins on hydrolysis yield only amino acids or their derivatives.

Examples:

(i) **Globulins** are insoluble in water but soluble in dilute salt solutions. They are found in animals, e.g. lactoglobulin is found in muscles and also in plants.
(ii) **Legumin and collagen** proteins are present in the connective tissues throughout the body. They are the most abundant proteins in the animal kingdom forming some 25 to 35% of body protein.
(iii) **Albumin** is the principal component of egg white and are soluble in water and dilute salt solutions.

2. Compound or conjugated proteins

Those proteins which are attached or conjugated to some non-protein groups are called compound or conjugated proteins. The non–protein parts are called prosthetic groups.

Name of Protein	Prosthetic Group
Nucleoprotein	Nucleic acid
Glycoproteins	Sugars
Lipoproteins	Lipid, e.g., lecithin
Phosphoproteins	Phosphoric acid

Examples:

(i) Phospho-proteins are conjugated with phosphoric acid.
(ii) Lipoproteins are conjugated with lipid substances like lecithin, cholesterol and fatty acids.

3. Derived proteins

The protein which are derived from simple and conjugated proteins by action of heat, physical forces or chemical factors.

Examples:

Proteoses enzymes, peptones, oligopeptides, polypeptides, etc.

Complete Hydrolytic Decomposition
Protein → Proteose → Peptone → peptides → Amino acids

(b) Based on their functions

Based on their functions, proteins may be classified as

(i) regulatory or hormonal proteins (ii) Structural proteins
(iii) Transport proteins (iv) Genetic proteins, etc.

Protein	Function	Examples
Enzymes	Biological catalysts, vital to all living systems.	Trypsin, pepsin
Structural proteins	Proteins that hold living systems together.	Collagen
Hormones	Act as messengers.	Insulin
Transport proteins	Transport oxygen from lungs to tissues.	Haemoglobin
Protective proteins	Destroy any foreign substance released into the living system.	Gamma globulin
Toxins	Poisonous in nature.	Snake venom

Structure of Proteins

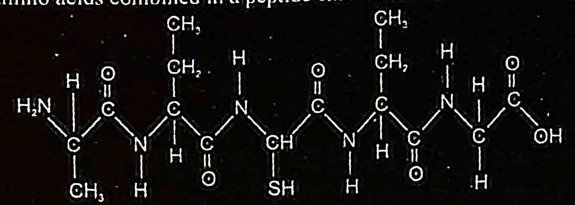
The majority of proteins are compact, highly convoluted molecules with the position of each atom relative to the others determined with great precision. To describe the structure of a protein in an organism, it is necessary to specify the

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three-dimensional shape that the polypeptide chain assumes. Proteins assume at least three levels of structural organization.

(i) Primary structure

The sequence of the amino acids combined in a peptide chain is called as the primary structure.



Primary structure of protein

(ii) Secondary structure

The secondary structure of a protein is a regular coiling or zigzagging of polypeptide chains caused by hydrogen bonding between NH and C=O groups of amino acids.

(iii) Tertiary structure

The three dimensional twisting and folding of the polypeptide chain results in the tertiary structure of proteins.

- **Some proteins also possess a fourth structure called the quaternary structure.**

Q12. What do you mean by denaturation of proteins?

Ans. **Denaturation of Proteins:**

The structure of the natural proteins is responsible for their biological activity. The structure of proteins can be disrupted easily by

(i) Heat (ii) Ultraviolet radiations (iii) Change in pH

(iv) Under strongly oxidizing or reducing conditions.

Under such conditions the proteins undergo denaturation.

For example:

The denaturation of albumin, the principal component of egg white, takes place when it is cooked. The helical structure of albumin disrupted.

Denaturation can be reversible or irreversible. The denaturation of albumin is irreversible.

Q14. Write down the importance of proteins?

Ans. **Biclogical Importance:**

(i) Proteins take an essential part in the formation of protoplasm which is the essence of all forms of life.

(ii) Nucleoproteins which are complexes of proteins with nucleic acids serve as carriers of heredity from one generation to the other.

(iii) Enzymes which are biological catalysts are protein in nature. Without them life is not possible.

(iv) Many proteins have specialized functions. Haemoglobin acts as a carrier of O_2. Some proteins act as hormones which have regulatory function. For example insulin and Thyroxine etc.

Industrially Importance:

(i) We are familiar with the use of leather made by tanning of hides. This is essentially a precipitation of the proteins with tannic acid.

(ii) Gelatin is obtained by heating bones, skin and tendons in water.

(iii) Caesein is another protein used in the manufacture of buttons and buckles.

(iv) It is used in bakery goods.

LIPIDS

"The naturally occurring organic compounds of animals and plants origin which are soluble in organic solvents and belong to a very heterogeneous group of substances are called lipids."

Meaning: The word lipid is derived from Greek, 'lipos' means fat.

Characteristics of lipids

1. They are insoluble in water and soluble in non-polar solvents e.g. ether, chloroform and benzene, etc.
2. Their primary building blocks are fatty acids, glycerol and sterols.
3. They are utilized by the living organisms.

There are three major "**food factors**" needed for human body.

(i) Proteins (ii) Carbohydrates (iii) Lipid (Fats and Oils)

Fats and oils are present in various types of foods and are of great nutritional value. Fats and oils are used in human diet. It also finds use as raw materials for the manufacture of soaps and detergents, paints, varnishes, polishes, cosmetic, printing inks and pharmaceuticals.

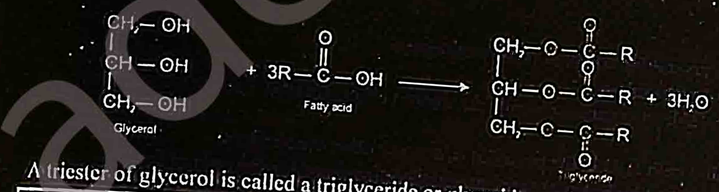
Sources of Fats and Oils

The main source of fats and oils are animals, plants and marine organisms.

- Animal fats are located particularly in adipose tissue cells. Butter and ghee are a special type of animal fats which are made from milk.
- Vegetable oils are chiefly present in seeds and nuts of plants.
- Marine oils are obtained from sea animals like salmons and whales.etc.

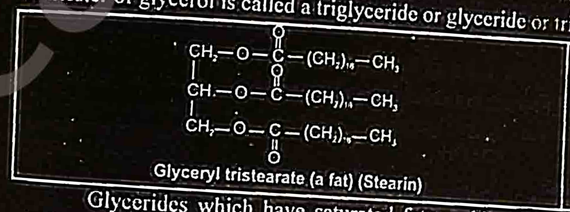
Structure and Composition of Fats and Oils

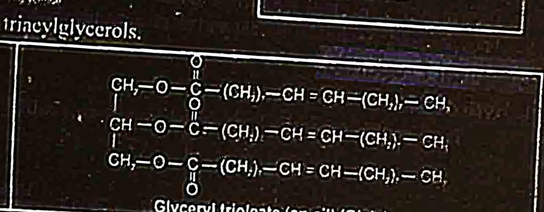
Animal and vegetable fats and oils have similar chemical structures. They are triesters formed from glycerol and long chain acids called fatty acids.



- Glycerol is commonly called as glycerine. It is trihydric alcohol.
- It is colorless oily fluid with sweetish taste.

A triester of glycerol is called a triglyceride or glyceride or trinoylglycerols.





Glycerides which have saturated fatty acids mostly solids or semi-solid are termed as fats. Glycerides having unsaturated fatty acids are mostly oils. The melting points of glycerides would depend on the extent of unsaturated fatty acid components in the molecule. The unsaturated glycerides have very low melting points and are liquids (oils). Saturated glycerides have higher melting points and are solids.

Qg. What are lipids? In What way fats and oils are different?

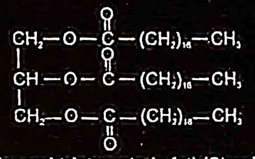
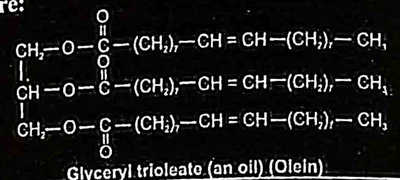
Ans. **Lipids**

Lipids are naturally occurring organic compounds of animals and plants origin which are soluble in organic solvents and belong to a very heterogeneous group of substances.

Differentiate between fats and oils

Fats	Oils
A glyceride in which the long chain saturated fatty acids predominate is called Fat.	A glyceride in which the long chain unsaturated fatty acids predominate is called Oil.
They are usually semi-solids or solids.	They are usually liquids.
They have high melting and boiling points.	They have low melting and boiling points.
Fats are generally obtained from animals.	Oils are generally obtained from plants and marine animals.

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Structure:	Structure:
	
Glyceryl tristearate (a fat) (Stearin)	Glyceryl trioleate (an oil) (Olein)

Classification of Lipids

Lipids are classified as:

1. Simple Lipids

These are esters of fatty acids with glycerol. For example, common fats and oils.

2. Compound Lipids

These contain radicals in addition to fatty acids and alcohol and include glycerol phospholipids, sphingolipids, lipoproteins and lipopolysaccharides.

3. Derived or Associated Lipids

They are the hydrolytic products of the above mentioned compounds. Sterols, vitamin D and terpenes belong to this class of lipids.

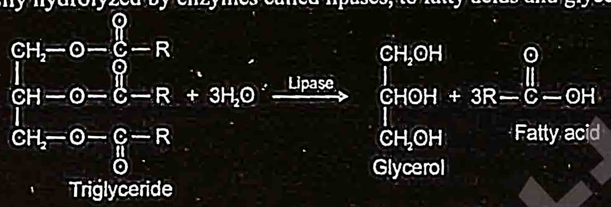
Physical Properties

1. Oils and fats may either be liquid or non-crystalline solids at room temperature.
2. When pure they are colourless, odourless and tasteless.
3. They are insoluble in water and readily soluble in organic solvents like diethyl ether, acetone, carbon tetrachloride and carbon disulphide.
4. They readily form emulsions when agitated with H_2O in the presence of soap or other emulsifiers.
5. They are poor conductor of heat and electricity and therefore serve as excellent insulator for the animal body.

Chemical Properties

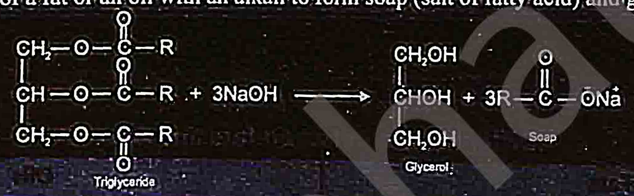
1. Hydrolysis

Triglycerides are easily hydrolyzed by enzymes called lipases, to fatty acids and glycerol.



2. Saponification

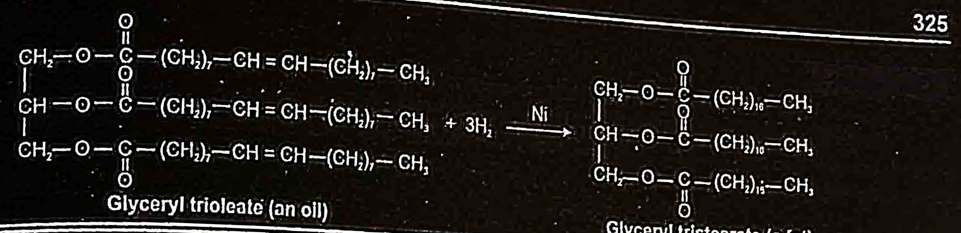
It is the hydrolysis of a fat or an oil with an alkali to form soap (salt of fatty acid) and glycerol.



3. Hardening of Oils

Unsaturated glycerides react with hydrogen in the presence of a metal catalyst to give saturated glycerides. The result is the conversion of a liquid glyceride (an oil) into a semi-solid glyceride (a fat).

This reaction is used commercially to harden vegetable oils into vegetable ghee or margarine. Hardened oils are extensively also used for making soaps and candles.

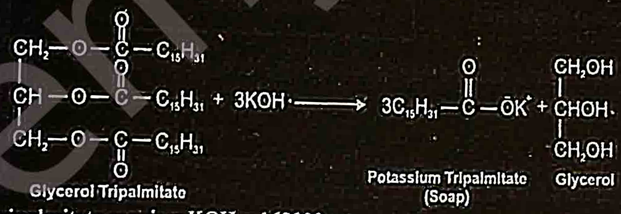


Q10. Define saponification number and iodine number. Discuss the term rancidity?

Saponification Number

"The number of milligrams of potassium hydroxide or sodium hydroxide required to saponify one gram of the fat or oil is called saponification number."

For example:



807g of glycerol tripalmitate requires KOH = 168000 mg

1g of glycerol tripalmitate requires $KOH = \frac{168000\,mg \times 1g}{807\,g} = 208\,mg$

Hence, the saponification number of glycerol tripalmitate is 208.

Signification:
It tells that a fat with high saponification number has short chain fatty acids and vice versa.

Rancidity of Fats or Oils

Fats or oils are liable to spoilage and give off an odour known as rancidity.

It is mainly caused by the hydrolytic or oxidative reactions which release foul smelling aldehydes and fatty acids.

Oils from sea animals which contain a relatively high proportion of unsaturated acid chains deteriorate rapidly.

Iodine Number

"The number of grams of iodine which will add to 100 grams of a fat or an oil is called iodine number."

The extent of unsaturation in a fat or an oil is expressed in terms of its iodine number. The value of iodine number depends on the number of double bonds present in the acid component of the glycerides. The glycerides with no double bonds have zero iodine number.

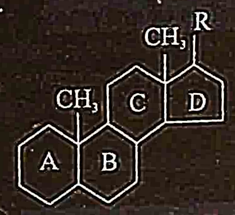
Acid Number

"The number of milligrams of potassium hydroxide required to neutralize one gram of fat is called acid number."

The acid number of a fat or an oil tells the amount of free fatty acids present in it.

Steroids

Steroids are naturally occurring lipids. Their parent nucleus has perhydrocyclopentanophenanthrene component which consists of three six-membered rings (A, B and C) and one five-membered ring (D). These rings are joined or fused to each other and have a total of 17-C atoms.



Structure of Steroid Nucleus

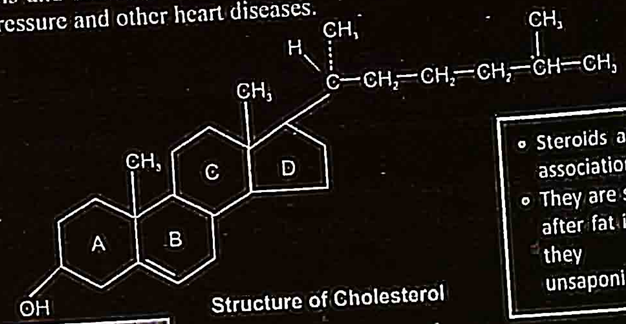
Very small variations in the bonding of atoms in the ring and in the groups attached to them give rise to compounds that are remarkably diverse in their biological functions. Some of the natural occurring compounds belonging to steroids are cholesterol, ergosterol, male and female sex hormones and the hormones of the adrenal cortex.

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1. Cholesterol

It is the most abundant animal sterol and occurs in all animal tissues but only in a few higher plants.

Cholesterol is present both in the free as well as esterified form in the blood, animal tissues, egg, yolk, various oils and fats and nerve tissues. Its increased quantities in blood make plaque like deposits in the arteries causing blood pressure and other heart diseases.



Structure of Cholesterol

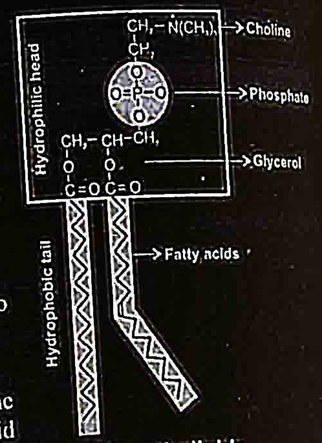
- Steroids are often found in association with fat.
- They are separated from fat after fat is saponified, since they occur as unsaponifiable residue.

2. Ergosterol

It is sterol of fungi and yeasts. When irradiated with ultraviolet rays, it is converted into ergocalciferol or vitamin D_2.

3. Phospholipids

Phospholipids have great biological importance. In the compounds, two of the hydroxyl groups are esterified with fatty acids and third forms a link with phosphoric acid or a derivative of phosphoric acid.



Phospholipids

Importance of lipids

(i) They are good source of energy and make the food more palatable.
(ii) They exert an insulating effect on the nervous tissues.
(iii) They are good energy reservoirs in the body.
(iv) Lipids are main part of cell protoplasm and cell membranes.
(v) Some lipids act as precursors of very important physiological compounds. For example, cholesterol is the precursor of steroid hormones.

Q12. What is the chemical nature of enzymes? Discuss the classification of enzymes?

ENZYMES

"The reaction catalysts of biological systems produced by living cells and are capable of catalyzing chemical reactions are called enzymes."

Typically enzymes are macromolecules with molecular masses ranging into millions.

Properties of enzymes

Two remarkable properties of enzymes are:

(i) Extraordinary specificity

Each enzyme catalyzes only one reaction or one group of closely related reactions.

(ii) Amazing efficiency

They may speed up reactions up to 10^{20}.

Substrate:
Substances on which enzyme acts to convert then into products are called substrates.

Composition of enzymes

Enzymes are either pure proteins or contain proteins as essential components and in addition require non-protein components which are also essential for their activity.

Apoenzyme

The protein component of the enzyme is called apoenzyme.

Exception To Protein Nature:
Ribozymes are few RNA molecules with enzymatic activity and are non–protein in nature.

Coenzyme / Prosthetic Group

The non-protein component is called the co-factor or co-enzyme.

Enzyme	Co-factor	Nature
Carbonic anhydrase	Zn^{2+}	Inorganic ion
Chrome oxidase	Fe^{2+}	Inorganic ion
Glucose 6- phosphatase	Mg^{2+}	Inorganic ion
Nicotinamide adenine dinucleotide	Nicotinamide vitamin	Organic compound
Thiamine pyrophosphatase	Vitamin B_1	Organic compound

Nomenclature of Enzymes

While naming the enzymes, suffix-"ase" is added to the name of the substrate on which the enzyme acts.

For example: Urease, sucrase, cellulase are the enzymes, which act upon the substrates urea, sucrose and cellulose respectively.

Complete structure of apoenzyme and prosthetic group is called as holoenzyme.
Apoenzyme + Co-enzyme = Holoenzyme
(Protein part) (Prosthetic group)

Classification of Enzyme

International Union of Bio-Chemistry (IUB) classified enzymes into six main types.

1. Oxidoreductases

These enzymes catalyze oxidation-reduction reactions.

Examples: Oxidase, dehydrogenase and peroxydase.

2. Transferases

These enzymes bring about an exchange of the functional group such as phosphate or acyl between two compounds.

Example: Phospho-transferases, etc.

3. Hydrolases

These enzymes catalyze hydrolysis.

Example: They include proteases called protolytic enzymes

4. Lyases

These enzymes catalyze the addition of ammonia, water or carbon dioxide to double bonds or removal of these to form double bonds.

Examples: Phospho-glyceromutases.

5. Isomerases

These enzymes catalyze the transfer of groups within molecules to yield isomeric forms of the substrate.

Example: Conversion of fumaric acid to maleic acid in the presence of fumarase enzyme.

6. Ligases

These enzymes link two molecules together through the breaking of high energy bonds.

Examples: Acetyl – S – COH, a carboxylase and succinic thiokinase.

Properties of Enzymes

1. Specificity

Enzymes are specific in their action which means that an enzyme will act on only one substrate or a group of closely related substrates. For example, hexokinase catalyses the conversion of hexoses like glucose, fructose and mannose to their 6-phosphate derivatives but glucokinase is specific for glucose only.

2. Protein Nature

Enzymes with few exceptions are protein in nature. They are produced by living cells but act in vivo as well as in vitro.

3. Direction of Enzyme Reactions

Most enzymatic reactions are reversible i.e. the same enzyme can catalyze reactions in both directions.

4. Isoenzymes

These are the enzymes from the same organisms which catalyze the same reaction but are chemically and physically distinct from each other.

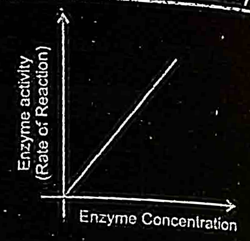
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Factors Affecting Enzyme Activity

(i) Enzyme Concentration

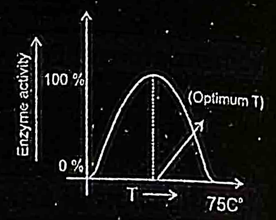
The rate of an enzymatic reaction is directly proportional to the concentration of the substrate.

The rate of reaction is also directly proportional to the square root of the concentration of enzyme. It means that the rate of reaction also increases with the increasing concentration of enzyme.



(ii) Temperature

The enzymatic reaction occurs best at or around 37°C which is the average normal body temperature. The rate of chemical reactions is increased by a rise in temperature but this is true only over a limited range of temperature. The enzymes usually destroy at high temperature. The activity of enzymes is reduced at low temperature. The temperature at which an enzyme reaction occurs the fastest, is called its optimum temperature.



(iii) Effect of pH

Just like temperature, there is also an optimum pH at which an enzyme will catalyze the reaction at the maximum rate. For example, the optimum pH of salivary amylase is 6.4 to 6.9.

(iv) Other Substances

The enzyme action is also increased or decreased in the presence of some other substances such as co-enzymes, activators and inhibitors. For example, some enzymes consist of simple proteins only such as insulin. Most of the enzymes are, the combination of a co-enzyme and an apo-enzyme.

Activators are the inorganic substances which increase the enzyme activity. For example; Mg^{2+} and Zn^{2+} ions are the activators of phosphatase and carbonic anhydrase enzymes respectively.

Inhibitors are the substances which reduce the enzyme activity.

(v) Radiation

Generally enzymes are readily inactivated by exposure to ultraviolet light, beta rays, gamma rays and X-rays.

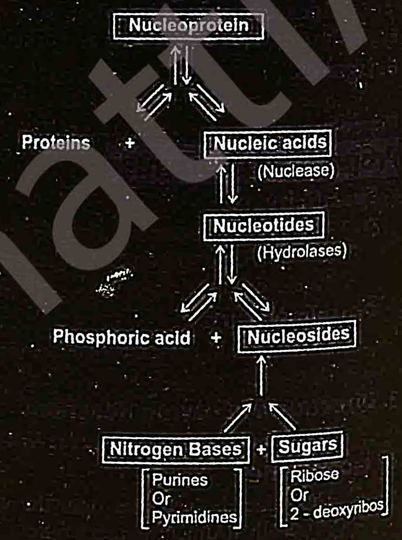
Importance of Enzymes

Enzymes are of great biological importance and are of great help in the diagnosis of certain diseases and have proved very useful as drugs.

Examples:

(i) **Alkaline phosphatase** is raised in rickets and obstructive jaundice.
(ii) **Lactic dehydrogenase or LDH-I** is raised in heart diseases.
(iii) **Thrombin** is used locally to stop bleeding.
(iv) **L–asparaginase** has proved very useful in the treatment of blood cancer in children.

Enzymes	Reaction catalyzed
Urease	Urea → $CO_2 + NH_3$
Invertase	Sucrose → Glucose + Fructose
Maltase	Maltose → 2 Glucose
Amylase	Starch → n Glucose
Pepsin	Proteins → Polypeptides → α-Amino acids
Trypsin	Polypeptides → α-Amino acids
Carbonic anhydrase	$H_2CO_3 \rightarrow H_2O + CO_2$
Nuclease	DNA, RNA → Nucleotides
Lactase	Lactose → Glucose + Galactose
Emulsin	Cellulose → n Glucose
RNA Polymerase	Ribo nucleotide triphosphates → RNA
DNA Polymerase	Deoxy nucleotide triphosphate → DNA

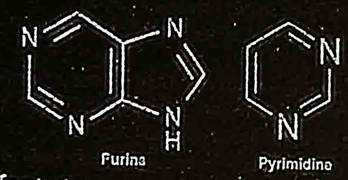


NUCLEIC ACIDS

- Nucleic acids were first demonstrated in the nuclei of pus cells in 1868 and in sperm heads in 1872 by Friedrick Miescher.
- They are present in every living cell as well as in viruses and have been found to be the essential components of the genes.
- They contain in their structure the blue prints for the normal growth and development of each and every living organism.
- The nucleic acids are responsible for the two fundamental functions which are common to all living organisms, these are (a) their ability to reproduce, store and transmit genetic information and (b) to undergo mutation.
- Two types of nucleic acids have been discovered, deoxyribonucleic acid (DNA) and ribonucleic acid (RNA).
- In the body nucleic acids occur as part of the conjugated proteins called nucleoproteins. The nucleic acids direct the synthesis of proteins.
- Cancer research involves an extensive study of nucleic acids.

Components of Nucleic Acids

- Both DNA and RNA are formed by joining together a large number of nucleotide units or mononucleotides units, each of which is a nitrogenous base - sugar phosphoric acid complex.
- Nitrogenous bases are either purine or pyrimidine derivatives. Purines include adenine and guanine whereas pyrimidines include, cytosine, uracil and thyamine.
- A nucleoside is a combination of nitrogenous base (purine or a pyramidine) with a sugar (ribo or deoxyribose). Depending upon the presence of ribo or a deoxyribo, nucleoside can either be a ribonucleoside or deoxyribonucleoside.
- Deoxyribonucleic acid (DNA) carries the genetic information and ribonucleic acid (RNA) is involved in putting this information to work in the cell.



Furina Pyrimidine

Nucleoproteins = Nucleic acid + Proteins
Base + Sugar → Nucleoside
Base + Sugar – PO_4^- = Nucleotides

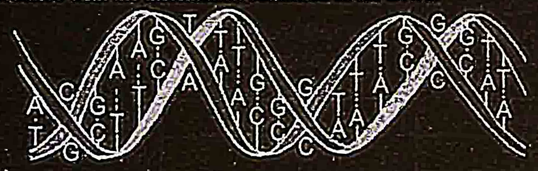
DNA and RNA differ in three ways.

(i) The sugar in RNA is ribose while the sugar in DNA is 2-deoxyribose.
(ii) Four different bases are found in DNA cytosine (C), thymine (T), adenine (A) and guanine (G). In RNA, thymine does not occur and its place is taken by uracil (U).
(iii) DNA is nearly always double stranded, while RNA is usually single stranded.

Watson and Crick Model of DNA

The key to the ability of DNA to preserve genetic information and to pass it on from generation to generation is its double-stranded structure, first deducted by James Watson and Francis Crick in 1953. This was the discovery that initiated the field of molecular biology.

Watson and Crick noticed that the double stranded structure provides a mechanism whereby the genetic information can be duplicated. This process is called replication. The synthesis of a polypeptide (protein) involves a series of events which occur in accordance with the information contained in the DNA.



Double Helical Structure

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Q16. Differentiate between DNA and RNA?

DNA	RNA
DNA stands for Deoxyribonucleic acid	RNA stands for Ribonucleic acid.
The sugar used in the structure of DNA is 2-deoxyribose.	The sugar used in the structure of RNA ribose.
It contains nitrogenous bases i.e. Cytosine, thyamine, adenine and guanine.	It contains nitrogenous bases i.e. Cytosine, and uracil, adenine and guanine.
It is double stranded.	Usually, RNA is single stranded.
It carries the genetic information in the cell.	It is involved in putting the genetic information to work in the cell.

KEY TERMS

1. Macromolecules are large molecules built up from small units called monomers.
2. The organic macromolecules are biological and non-biological in nature.
3. Biological macromolecules are called life molecules and non-biological are man made synthetic polymers.
4. The polymer chains may be linear, branched or cross-linked.
5. A thermoplastic polymer is the one which can be softened and hardened by heating and cooling respectively.
6. A thermosetting polymer is one which becomes permanently hard on heating.
7. The polymerization process involves addition and condensation reactions.
8. The formation of polyethene is an example of addition polymerization.
9. Nylon, a polyamide and terylene, a polyester, are examples of condensation polymers.
10. Carbohydrates, proteins, fats, and nuclei acids are natural macromolecules.
11. Carbohydrates are the most abundant biomolecules on earth. They are classified into monosaccharides, oligosaccharides and polysaccharides.
12. Proteins are the essential components of all living organisms. They are the polymers of amino acids.
13. Lipids are naturally occurring organic compounds of animal and plant origin and they are soluble in organic solvents. Fats and oils are the most important lipids found in nature.
14. Enzymes are proteins that catalyze chemical reactions in living organisms. They are very specific in their action.

SOLVED OBJECTIVE EXERCISE

Q1. Fill in the blanks.

(i) Macromolecules are built up from small units called _____.
(ii) Nylon is a polyamide and terylene is a _____.
(iii) Nylon is prepared by the reaction of _____ and hexamethylenediamine.
(iv) Based on their thermal properties, plastics are divided into _____ main classes.
(v) Polyvinyl chloride is a _____ plastic.
(vi) Glucose is stored as _____ in the liver.
(vii) Glucose and fructose are water _____ carbohydrates.
(viii) Protein after digestion changes to _____.
(ix) Purine and pyrimidine are _____ of nucleic acids.
(x) Addition of a plasticizer _____ the flexibility of the polymer.

Answer Key.

(i)	Monomers	(ii)	Polyester	(iii)	Adipic acid
(iv)	Two	(v)	Thermo	(vi)	Glycogen
(vii)	Soluble	(viii)	Amino acids	(ix)	Nitrogenous bases
(x)	Improves				

Q2. Indicate True or false.

(i) Nylon 6,6 and terylene are condensation polymers.
(ii) The disposal of plastics does not cause any pollution problem.
(iii) Fructose is a polysaccharide carbohydrate.
(iv) Human beings get no food nutrient from cellulose.
(v) The most abundant and the most important steroid in the human body is vitamin D
(vi) Enzymes are the compounds containing C,H and O only.
(vii) The degree of unsaturation of fats is measured by their iodine number.
(viii) Activity of an enzyme varies with temperature and pH
(ix) Nucleic acids are biological catalysts.
(x) The nucleic acids are responsible for protein synthesis in the human body.

Answer Key.

(i)	True	(ii)	False	(iii)	False	(iv)	True	(v)	False
(vi)	False	(vii)	True	(viii)	True	(ix)	False	(x)	True

Q3. Multiple choice questions. Encircle the correct answer.

(i) In which of these processes are small organic molecules made into macromolecules.
(a) the cracking of petroleum fractions (b) the fractional distillation of crude oil
(c) the polymerization of ethene (d) the hydrolysis of proteins

(ii) Which of these polymers is an addition polymer?
(a) Nylon -6,6 (b) polystyrene (c) terylene (d) epoxy resin

(iii) Which of these polymers is a synthetic polymer?
(a) animal fat (b) starch (c) cellulose (d) polyester

(iv) Plastics cause pollution problem because many plastics.
(a) are made from petroleum (b) are very inflammable
(c) burn to produce toxic fumes (d) decompose to produce toxic products.

(v) The fibre which is made from acrylonitrile as monomer:
(a) PVC (b) rayon fibre (c) acrylic fibre (d) polyester fibre

(vi) A polymeric substance that is formed in the liquid state and then hardened to a rigid solid is called as
(a) fibre (b) plastic (c) varnish (d) polyamide resin

(vii) Vegetable oils are
(a) unsaturated fatty acids (b) glycerides of unsaturated fatty acids
(c) glycerides of saturated fatty acids (d) essential oils obtained from plants

(viii) Which one of the following elements in not present in all proteins?
(a) carbon (b) hydrogen (c) nitrogen (d) sulphur

(ix) Which one of the following is a water soluble vitamin?
(a) niacin (b) riboflavin (c) trypsin (d) ascorbic acid

(x) Which one of the following enzymes brings about the hydrolysis of fats?
(a) urease (b) maltase (c) zymase (d) lipase

(xi) The reaction between fat and NaOH is called.
(a) esterification (b) hydrogenolysis (c) fermentation (d) saponification

(xii) Which one of the following statements about glucose and sucrose is incorrect?
(a) both are soluble in water (b) both are naturally occurring
(c) both are carbohydrates (d) both are disaccharides

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Solved Exercise MCQs

Q.No	Answer	Reason
(i)	(c) The polymerization of ethene	$n\ CH_2 = CH_2 \xrightarrow[\text{100 atm pressure, traces of } O_2\ (0.1\%)]{400°C} \text{Polyethylene}$
(ii)	(b) Polystyrene	$n\ CH_2 = CH(C_6H_5) \longrightarrow$ Styrene → Polystyrene
(iii)	(d) Polyester	As polyester is man made polymer.
(iv)	(d) decompose to produce toxic products	These toxic products causes air pollution.
(v)	(c) acrylic fibre	$n\ CH_2 = CH(CN) \longrightarrow$
(vi)	(b) Plastic	Plastic become softened on heating and hardened when cooled.
(vii)	(b) glycerides of unsaturated fatty acids	They convert into glycerides of saturated fatty acids (ghee) by hydrogenation.
(viii)	(d) Sulphur	Sulphur is not essential element of protein while others are essential.
(ix)	(d) Ascorbic acid	Ascorbic acid is vitamin C.
(x)	(d) lipase	Tryglycerides are easily hydrolyzed by lipase to fatty acids and glycerol.
(xi)	(d) Saponification	In this reaction soap is formed.
(xii)	(d) both are disaccharides	Sucrose is disaccharide glucose is not.

SOLVED ANSWERS TO EXERCISE

Q6. What is the repeating unit in each of the following polymers?
(a) Polystyrene (b) Nylon-6,6 (c) Teflon (d) Orlon

Ans. Repeating units in following polymers:

No.	Polymer	Repeating Unit
(a)	Polystyrene	Styrene ($H_2C = CH - C_6H_5$)
(b)	Nylon - 6, 6	∘ Adipic acid (Hexanedioic acid) $HOOC - (CH_2)_4 - COOH$ ∘ Hexamethylenediamine $H_2N - (CH_2)_6 - NH_2$
(c)	Teflon	$C = C(F)(F)$ Tetrafloroethylene
(d)	Orlon	$CH_2 = CH - CN$ Acrylonitrile

Q8. Point out one difference between the compounds in each of the following pairs.
(a) Glucose and fructose (b) Sucrose and maltose (c) Cellulose and starch

Ans. (a) Glucose and Fructose:

Glucose	Fructose
Glucose is an Aldohexose containing aldehydic group (-C(=O)-H)	Fructose is a ketohexose containing ketonic group (-C(=O)-)
Its cylic structure contains hexagonal ring i.e. having six corners.	Its cyclic structure contains pentagonal ring i.e. having five corners.

(b) Sucrose and Maltose:

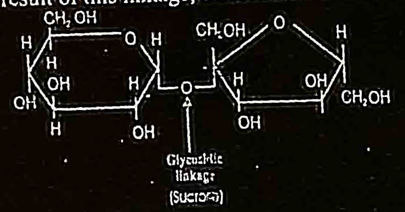
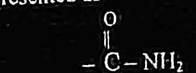
Sucrose	Maltose
Sucrose is a disaccharide of α-D-Glucose and fructose. Glycosidic Linkage. Sucrose	Maltose is a disaccharide of two α-D-Glucose and fructose. Maltose

(c) Differentiate between cellulose and starch:

Cellulose	Starch
(i) Cellulose is the carbohydrate produced by plants but not digested by human diet	(i) Strach is obtained from plants and are used in human diet.
(ii) It is the polymer of β-D-Glucose.	(ii) It is the polymer of α-D-glucose
(iii) It is an unbranched polymer.	(iii) It may form branched structure.

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Q11. What is the difference between a glycoside linkage and a peptide linkage?

Glycosidic Linkage	Peptide Linkage
1. The linkage formed between two monomers of carbohydrates is called Glycosidic linkage. 2. It is represented as $-C-O-C-$ 3. As a result of this linkage, disaccharide is formed.  Glycosidic linkage (Sucrose)	1. The linkage formed between two amino acid is called peptide linkage. 2. It is represented as  3. As a result of peptide linkage, peptide is formed.  Peptide linkage (Dipeptide)

Previous Board Questions

1. Define Carbohydrates. Classify them. Give one examples of each.
2. What do you mean by Rancidity of Fats or Oils?
3. What are enzymes? Give their any two types.
4. What are fatty acids? Give on example.
5. Write open chain structure of:
   (a) Glucose (b) Fructose
6. What are lipids?
7. What is the effect of these factors upon reactivity of Enzymes:
   (a) Radiation (b) Enzyme concentration.
8. Differentiate between thermoplastic and thermosetting polymers.
9. What are saponification number and iodine number?
10. How polystyrene is prepared? Give its two uses.
11. Write down the structure of cholesterol.
12. Write down the chemical nature of enzyme.
13. What is starch? Differentiate between amylose and amylopectin.
14. Write down uses of proteins.
15. Write cyclic structures of glucose.
16. How are the polymers classified on the basis of thermal properties?
17. What are steroids? Give their general structure.
18. What are polyamides? Give the formation of Nylon 6, 6.
19. Differentiate between Glucose and Fructose.

For Answers Study
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CHAPTER 15

COMMON CHEMICAL INDUSTRIES IN PAKISTAN

Introduction

At the time of independence in 1947, Pakistan had an almost negligible industrial base. For the past 55 years, the Country has undergone a structural change from a purely agrarian economy to a semi-chemical industrial state. Pakistan is now making many household products like, soap, detergents, glasses, plastics, fibres, paint varnish etc. Heavy industry like iron, cement, fertilizer, paper, and textile are also on the road of development.

The natural resources are being exhausted with growing population and increase in the standard of living all over the world. To meet this situation, the scientists and technologists are busy in the development of the substitute materials from cheaper and reusable sources e.g., the natural fibers like cotton, silk, wool cannot meet the clothing requirements of the world; therefore, scientists have developed the artificial fibres.

Similarly, crop yield has been increased by the development of the fertilizers, pesticides and herbicides to meet the world food requirements. All these materials require their chemical preparation on industrial scales. In fact the magnitude of chemical industry of a country is a measure of its economic development and progress. Different chemical industries such as fertilizer, cement and paper are developing very fast in Pakistan.

FERTILIZERS

Early History

Agriculture is one of the oldest industry known to man. The use of manure as a fertilizer dates back to the beginning of agriculture. Since 5000 B.C. the Chinese used animal manure as fertilizer.

Manure

"A manure is an organic material used to fertilize land and it usually consists of faeces and urine of domestic livestock."

Q.5 (a) What are fertilizers? Why are they needed?

Ans **Fertilizers**

The substances which are added to the soil to make up the deficiency of essential elements like nitrogen, phosphorus and potassium (NPK) required for the proper growth of plants are called fertilizers.

Examples: Urea, KNO_3, manure, NH_3, $(NH_4)_2HPO_4$ etc.

Need of Fertilizers

Fertilizers enhance the natural fertility of the soil or replenish the chemical elements taken up from soil by the previous crops.

Elements Essential for Plant Growth

Plants need nutrients from the soil for a healthy growth. The elements essential for the plant growth can be classified into two classes; micro-nutrients and macro-nutrients.

Q. Differentiate between micronutrients and macronutrients.

Ans

Micronutrients	Macronutrients
• The nutrients which are required in a very small amount for the growth of plants are called micro-nutrients.	• The nutrients which are required in a very large amount for the growth of plants are called macro-nutrients.

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• These includes B, Cu, Fe, Mn, Zn, Mo and Chlorine	• These includes N, P, K, Ca, Mg, S, C, H and O
• These are generally required in quantities ranging from 6g to 200g per acre.	• These are generally required in quantities ranging from 5kg to 200 kg per acre.

Requirement of a fertilizer

- Every compound of the desired elements can not be a fertilizer.
- The desired elements should be present in the compound in a water soluble form (so that the plant can take it up) readily available to the plants.
- The compound employed as fertilizer should be stable in soil as well as in storage e.g., it should not be deliquescent or set to hard stony materials with time. Above all it should be cheap to manufacture.

Q.6c Write down the essential qualities of a good fertilizer.

Essential qualities of a good fertilizer

The essential requisites of a good fertilizer are:

1. The nutrient elements present in it must be readily available to the plant.
2. It must be fairly soluble in water so that it thoroughly mixes with the soil.
3. It should not be injurious to plant.
4. It should be cheap.
5. It must be stable so that it is available for a longer time to the growing plant.
6. It should not alter the pH of the soil.
7. By rain or water, it should be converted into a form, which the plant can assimilate easily.
8. It should provide the entire nutrient necessary for the growth of a plant.
9. It should not be deliquescent or set to hard stony mass with time.

Q.5b Discuss the classification of fertilizers and their uses.

Classification of Fertilizers

Fertilizers are classified according to the nature of the elements like nitrogen, phosphorus and potassium which they provide to the soil. This classification gives the following types of fertilizers.

(i) Nitrogenous fertilizers
(ii) Phosphatic fertilizers
(ii) Potassium fertilizers

Q. What are nitrogenous fertilizers? Write down note on role of N_2 in plant growth.

(i) Nitrogenous fertilizers

Those fertilizers which supply nitrogen to the plants or soil are called nitrogenous fertilizers.

Examples

Ammonium sulphate, Calcium ammonium nitrate, Basic calcium nitrate, Calcium cyanamide, Ammonia, Ammonium nitrate, Ammonium phosphate, Ammonium chloride and urea.

Role of nitrogen in plant growth

(i) Nitrogen is required during the early stages of plant growth for the development of stems and leaves.
(ii) It is the main constituent of protein.
(iii) It imparts green colour to the leaves.
(iv) It enhances the yield and quality of the plants.

(a) Ammonia (NH_3) as a Fertilizer

Ammonia is used in liquid state while all other nitrogen fertilizers are used in the solid form. Anhydrous ammonia has become an important fertilizer for direct application to soil. Ammonia contains 82% nitrogen and it is injected about 6 inches under the surface of the soil, to avoid it from seeping out.

All the nitrogen fertilizers make the soil acidic, except potassium nitrate KNO_3, sodium nitrate $NaNO_3$ and Calcium nitrate $Ca(NO_3)_2$ but this acidity of the soil can be controlled through liming of the soil (by the addition of lime) at regular intervals.

Q.5c How is urea manufactured in Pakistan? Describe in detail the process used.

Urea

$(NH_2)_2CO$
Aminomethanamide

Urea is a high quality nitrogenous fertilizer. It contains about 46% nitrogen and is the most concentrated solid nitrogen fertilizer. It is most widely used nitrogen fertilizer in Pakistan.

Manufacturing Process

Urea is produced by the reaction of liquid ammonia with gaseous carbon dioxide. Following steps are involved in the manufacture of urea.

(i) Preparation of Hydrogen
(ii) Preparation of Ammonia
(iii) Preparation of Ammonium Carbamate
(iv) Preparatin of Urea
(v) Concentration of Urea
(vi) Prilling

Preparation of Ammonium Carbamate

Gaseous CO_2 is mixed with ammonia in the volume ratio of 1:2 in a reactor to produce ammonium carbamate

$$CO_{2(g)} + 2NH_{3(g)} \longrightarrow NH_2 - \overset{\overset{O}{\|}}{C} - O - NH_4$$

Ammonium Carbamate

Preparation of Urea

Dehydration of ammonium carbamate gives urea.

$$NH_2 - \overset{\overset{O}{\|}}{C} - O - NH_4 \xrightarrow{\Delta} NH_2 - \overset{\overset{O}{\|}}{C} - NH_2 + H_2O$$

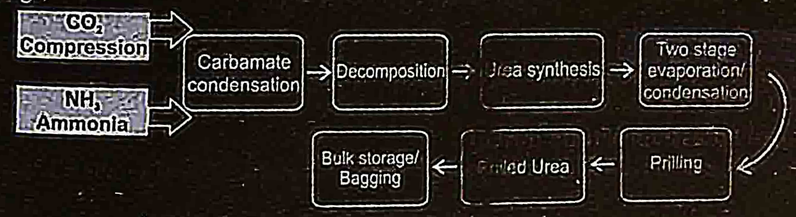
Urea

Concentration of Urea Solution

The urea solution is concentrated in an evaporation section where water is evaporated by heating with steam under vacuum in two evaporation stages whereby 99.7% urea melt is obtained. It is then pumped to prilling tower.

Prilling

The molten urea is sprayed at the prilling tower by means of prilling bucket where it is cooled by the air rising upward. Molten droplets solidify into the form of prills. Urea prills thus produced are either sent to the bagging section or to the bulk storage.



Flow sheet diagram for manufacture of area

(c) Ammonium Nitrate (NH_4NO_3)

It is manufactured by the neutralization reaction between ammonia and nitric acid as given below.

$$NH_{3(g)} + HNO_{3(g)} \longrightarrow NH_4NO_{3(s)}$$

After neutralization, the water is evaporated. The solid ammonium nitrate is melted and then sprayed down from a tall tower. The falling droplets are dried by an upward current of air. The fertilizer solidifies as tiny, hard pellets called

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prills. Prills of fertilizers are free of dust, easy to handle and easy to spared on the field. Ammonium nitrate contains 33-33.5% nitrogen. It is hygroscopic in nature.

Uses

- It is a useful fertilizer for many crops except paddy rice because the microbial bacteria in flooded fields decompose it to nitrogen gas (which escapes in air).
- It is also used in combination with limestone.

Q.4 What are phosphatic fertilizers? How are they prepared? Mention the role of phosphorus in the growth of plants.

(ii) Phosphatic fertilizers

Those fertilizers which provide phosphorus to the plants or soil are called phosphatic fertilizers.

Examples

The two most important water soluble fertilizers are

(i) Super phosphate (calcium super phosphate) $Ca(H_2PO_4)_2$

(ii) Triple phosphate (diammonium-phosphate) $(NH_4)_2HPO_4$ or DAP

The various phosphatic fertilizers have different compositions, due to which they have different solubilities.

Preparation of Diammonium Phosphate $(NH_4)_2HPO_4$

Anhydrous ammonia gas is reacted with pure phosphoric acid to prepare diammonium phosphate by a continuous process at 60 – 70°C and pH 5.8 to 6.

$$2NH_{3(g)} + H_3PO_{4(\ell)} \longrightarrow (NH_4)_2HPO_4 + \text{Heat}$$

It is an exothermic reaction. The heat of reaction vaporizes water from the liquor and the crystals of diammonium phosphate are taken out, centrifuged, washed and dried. It contains **16% nitrogen** and **48% P_2O_5**. This product contains about **75% plant nutrients** and is deemed suitable for use either alone or in mixed with other fertilizers.

Role of Phosphorus in Plant Growth

(i) Phosphorus is required to stimulate early growth, to accelerate the seed and fruit formation during the later stages of growth.

(ii) It also increases the resistance to diseases.

(iii) Potassium fertilizers

Those fertilizers which provide potassium to the plants or soil are called potassium fertilizers.

Example: KNO_3

Preparation of Potassium Nitrate (KNO_3)

On industrial scale, it is prepared by the double decomposition reaction between sodium nitrate and potassium chloride.

$$NaNO_{3(aq)} + KCl_{(aq)} \longrightarrow NaCl_{(aq)} + KNO_{3(aq)}$$

A concentrated hot solution of sodium nitrate is prepared and solid potassium chloride is added into it. On heating, the potassium chloride crystals change into sodium chloride crystals, and the hot potassium nitrate is run through the sodium chloride crystals at the bottom of the kettle. A little water is added to prevent further deposition of sodium chloride as the solution is cooled, which results into a good yield of pale yellow solid potassium nitrate. It contains 13% nitrogen and 44% potash.

Role of Potassium in plant growth

(i) Potassium is required for the formation of starch, sugar and the fibrous material of the plant.

(ii) They increase resistance to diseases and make the plants strong by helping in healthy root development.

(iii) They also help in ripening of seeds, fruits and cereals.

(iv) Potassium fertilizers are especially useful for tobacco, coffee, potato and corn.

Q.6 (a) What are prospects of fertilizer industry in Pakistan?

Ans

Fertilizer Industry in Pakistan

Pakistan is essentially an agricultural country. Due to repeated cultivation of crops and to increase the potential of land, fertilizers are gaining importance. Urea is the most important fertilizer used in Pakistan.

Government of Pakistan is trying to increase the production of fertilizers and reduce the gap between demand and supply. At present, there are about 14 fertilizer plants working in private as well as government sector. The total production of urea fertilizer in 2002 in Pakistan is about **56, 30,100 metric tons per annum.**

CEMENT

Definition

"Cement is the material obtained by burning an intimate mixture of calcarious and argillaceous materials at sufficiently high temperature to produce clinkers. These clinkers are then ground to a fine powder called cement or Portland cement."

The essential constituents are lime (obtained from limestone) silica and alumina (present in clay).

Portland Cement

Cement was first introduced by an English Mason Joseph Aspdin. He found it when strongly heated mixture of limestone and clay was mixed with water and allowed to stand, it hardened to a stone like mass which resembled Portland rock, a famous building stone of England. Since then the name of **Portland Cement** is given to the mixture of lime (obtained from limestone), silica, iron oxide and alumina.

Q.7a Describe the composition of a good portland cement.

Average composition of good sample of Portland Cement

Compound	%age
Lime (CaO)	62
Silica (SiO_2)	22
Alumina (Al_2O_3)	7.5
Magnesia (MgO)	2.5
Iron oxide (Fe_2O_3)	2.5
Sulphur trioxide (SO_3)	1.5
Sodium oxide (Na_2O)	1.0
Potassium oxide (K_2O)	1.0

Q. Write down Raw Material necessary for the manufacture of cement.

Raw Materials

The important raw materials used for the manufacture of cement are:

(i) **Calcarious material** (limestone, marble, chalks, marine shell) as source of lime (CaO).

(ii) **Argillaceous material** (clay, shale, slate, blast furnace slag). They provide acidic components such as aluminates and silicates.

(iii) **Gypsum** (2%) is used to increase the setting time.

Manufacturing Process of Cement

The manufacturing process of cement involves either a dry process or a wet process. The choice of dry or we process, depends on the followings factors.

(i) Physical condition of the raw materials.

(ii) Local climatic conditions of the factory.

(iii) The price of the fuel.

- In Pakistan, most of the factories use wet process for the production of cement.

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- Dry process needs excessive fine grinding and it is more suited for the hard material.
- Wet process, on the other hand, is free from dust, grinding is easier and the composition of the cement can easily be controlled.

Q7b. Discuss the wet process for the manufacturing of cement with the help of flow sheet diagram.

Wet Process

In this process grinding is done in the presence of water. There are five stages in the manufacture of Portland cement.

(i) Crushing and grinding of the raw material.
(ii) Mixing the material in correct proportion.
(iii) Heating the prepared mixture in a rotary kiln.
(iv) Grinding the heated product known as clinker.
(v) Mixing and grinding of cement clinker with gypsum.

(i) Crushing and Grinding

Soft raw materials are first crushed into a suitable size, often in two stages, and then ground in the presence of water, usually in rotating cylindrical ball or tube mills containing a charge of steel balls.

(ii) Mixing of the Raw Material

The powdered limestone is then mixed with the clay paste in proper proportion (limestone 75%, clay 25%); the mixture is finely ground and made homogeneous by means of compressed air mixing arrangement. The resulting material is known as slurry. The slurry, which contains 35 to 45% water, is sometimes filtered to reduce the water content from 20 to 30% and the filler cakes are stored in storage bins. This reduces the fuel consumption for heating stage.

(iii) Heating the Slurry in a Rotary Kiln

Raw meal or slurry prepared as above is introduced into the rotary kiln with the help of a conveyer. The rotary kiln consists of a large cylinder 8 to 15 feet in diameter and 300-500 feet in length. It is made of steel and is lined inside with firebricks. The kiln rotates horizontally on its axis at the rate of 1-2 revolution per minute and it is inclined a few degree. As the kiln rotates, the charge slowly moves downward due to the rotary motion.

Now the charge is heated by burning coal, oil or natural gas. In the rotary kiln the charge passes through the different zones of temperature where different reactions take place. The charge takes 2-3 hours to complete the journey in the kiln.

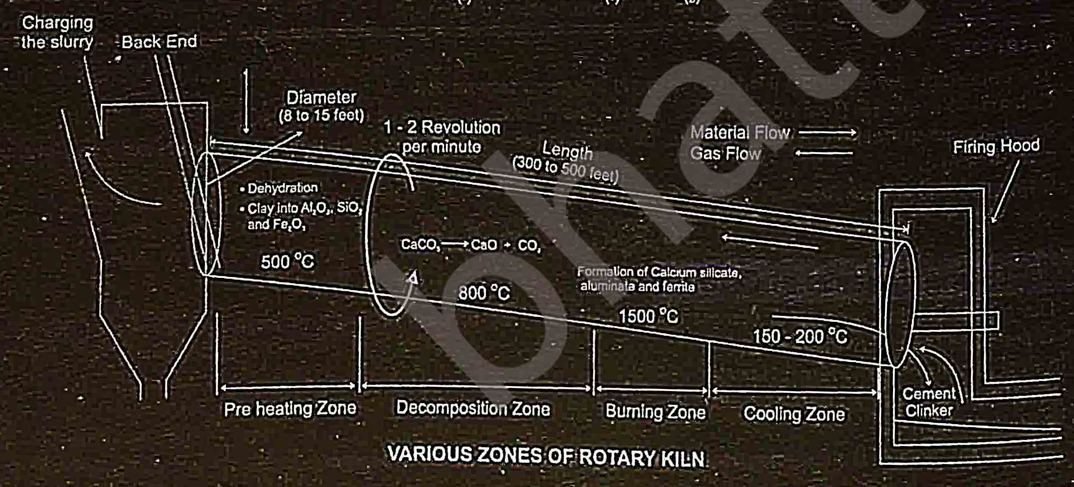
(a) Drying or Preheating Zone (Minimum temperature zone)

In this zone, the temperature is kept at 500°C, whereby the moisture is removed and the clay is broken into Al_2O_3, SiO_2, and Fe_2O_3.

(b) Decomposition Zone (Moderate temperature zone)

Here the temperature goes upto 900°C. In this zone the limestone ($CaCO_3$) decomposes into lime (CaO) and CO_2.

$$CaCO_{3(s)} \xrightarrow{900°C} CaO_{(s)} + CO_{2(g)}$$



VARIOUS ZONES OF ROTARY KILN

(c) Burning Zone (Maximum temperature zone)

In this zone, the temperature goes up to 1500°C and the oxides; e.g., CaO, SiO_2, Al_2O_3 and Fe_2O_3 combine together and form calcium silicate, calcium aluminate and calcium ferrite.

(d) Cooling Zone

This is the last stage in the kiln where the charge is cooled upto 150-200°C.

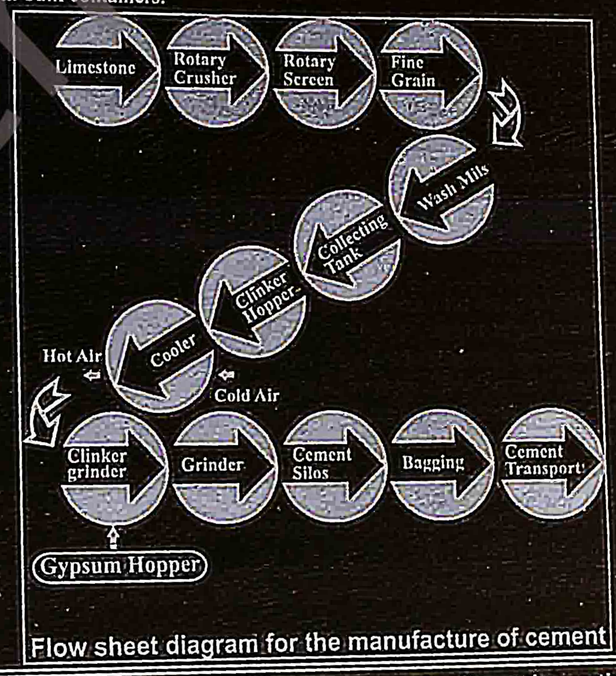
(vi) Clinker Formation

The resulting product obtained from the kiln is known as cement clinker. This has the appearance of greenish black or grey coloured balls varying in size from small nuts to peas.

(v) Grinding the Clinkers with Gypsum

The cement clinkers are then air-cooled. The required amount of gypsum (2.0%) is first ground to a fine powder and then mixed with clinkers. At this stage, finished cement is pumped pneumatically to storage silos from where it is drawn for packing in paper bags or for dispatch in bulk containers.

⇒ Pneumatically
air-powered, air-driven
⇒ Silos
A structure for storing Bulk materials.



Flow sheet diagram for the manufacture of cement

Q7c What do you understand by the term "setting of cement." Also discuss the reactions taking place in first 24 hours and between 1 to 7 days?

Setting of Cement

"Cement paste when combined with water and allowed to stand for sometime then the resulting mass becomes hard and very resistant to pressure. This process is known as setting of cement."

The use of cement in the construction of building is based on its property of setting to a hard mass. The reactions involved in the setting of cement are described as follows:

(a) Reactions Taking Place in First 24 Hours

A short time after the cement is mixed with water, tri-calcium aluminate absorbs water (hydration) and forms a colloidal gel of the composition, $3Ca.Al_2O_3.6H_2O$ (hydrated tri-calcium aluminate).

This gel starts crystallizing slowly, reacts with gypsum ($CaSO_4.2H_2O$) to form the crystals of calcium sulpho aluminate ($3CaO.Al_2O_3.3CaSO_4.2H_2O$).

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(b) Reactions Taking Place Between 1 to 7 Days

- Tri–calcium silicate ($3CaO.SiO_2$) and tricalcium aluminate ($3CaO.Al_2O_3$) get hydrolyzed to produce calcium hydroxide and aluminium hydroxide.
- The calcium hydroxide, thus formed, starts changing into needle-shaped crystals, which get studded in the colloidal gel and impart strength to it.
- Alumimin hydroxide, on the other hand, fills the interstices resulting in hardening the mass. The gel formed starts losing water partly by evaporation and sets to a hard mass.

Cement Industry in Pakistan

- At the time of partition in 1947, there were four cement plants in West Pakistan, which produced about 330,000 tons of cement every year.
- However in 1954 the production of cement went up to 660,000 tons.
- In 1956 two more cement factories were set up at **Daud Khel** and **Hyderabad**, but even then the production of cement was not enough to meet the increasing demand of the construction industry in the country.

For a developing country like Pakistan there is always an increasing need of cement for development projects. Efforts were thus made to build more factories. At present there are about **22 cement factories** in private as well as in public sectors, which are manufacturing cement both by dry and wet processes. The total production of these 22 cement plants is **9,578,802 metric tons/annum.**

PAPER INDUSTRY

Early History

- The word "paper" is derived from the name of a reedy plant "Papyrus". Which grew abundantly along the marshy Delta of the River Nile in Egypt around 3000 B.C.
- The invention of modern paper is credited to Ts'ai Lun of China, who, in 105 A.D, was an official attached to the Imperial Court of China. He prepared a sheet of paper using the bark of mulberry tree that was treated with lime and mixed with bamboo and other fibres to get the paper of desired properties.

Definition

"A sheet material made up of a network of natural cellulosic fibres which have been deposited from an aqueous suspension is called paper." The product obtained is a network of interwinning (interlocking) fibres.

Q. 8. What are the essential non-woody and woody raw materials used in the production of pulp and paper in Pakistan?

Ans: Raw Material

The main raw materials used in the production of pulp and paper in Pakistan is of two types, that is non-woody and woody raw materials.

Non-Woody Raw Materials				Woody Raw Materials	
(i)	Wheat straw	(vi)	Cotton stalk	(i)	Poplar (hard wood)
(ii)	Rice straw	(vii)	Cotton linter	(ii)	Eucalyptus (hard wood)
(iii)	Bagasse	(viii)	Kahi grass	(iii)	Douglas fir (soft wood)
(iv)	Bamboo	(ix)	Grasses		
(v)	Rag				

Q9. (a) What are the Principal methods of chemical pulping used for the production of paper.

Ans: Pulping processes

The following are three principal methods of chemical pulping and are used for the production of paper pulps.

1. Kraft process (Alkaline)
2. Sulphite process (Acidic)
3. Neutral Sulphite Semi Chemical process (NSSC)

The neutral sulphite semi chemical process has come to occupy the dominant position because of the advantages in chemical recovery and pulp strength. In this section, we will discuss only the **neutral sulphite semi chemical process**, which is mostly used in pulp and paper industry in Pakistan.

Q9. (b) Describe the neutral sulphite semi–chemical process for the manufacturing of pulp and paper.

Neutral Sulphite Semi-Chemical Process (NSSC)

Process Description

This process utilizes sodium sulphite cooking liquor which is buffered with sodium carbonate or NaOH to neutralize the organic acid liberated from the raw materials.

The non-woody raw materials which are used in this process; are wheat straw, rice straw, bagassse, cotton linter and rags. Wheat straw may be used alone or combined with other materials in different proportions. The essential steps in the process are as follows:

(i) Cutting of the raw materials (ii) Dry cleaning (iii) Wet cleaning
(iv) Screening (v) Digestion (vi) Blow tank
(vii) Pulp washing (viii) Bleaching (ix) Stock preparation plant
(x) Paper making machine

(i) Cutting of Raw Materials

The non-woody raw materials come in the precut state and are processed as such. But in the case of wood based raw materials, big logs are cut into small chips before further processing.

(ii) Dry Cleaning

Wheat straw is collected from the storage and is then sent for dry cleaning. For this purpose air is blown into the raw material, which removes unwanted particles.

(iii) Wet Cleaning

Dry wheat straw is then subjected to wet cleaning, which not only removes the remaining dust particles, but the soluble materials also get dissolved in water.

(iv) Screening

In most pulp and paper processes some type of screening operation is required to remove the over sized troublesome and unwanted particles.

- Magnetic separator removes iron pieces like nails and bolts, etc.
- Stones and other oversized pieces are removed by centri-cleaners.

The major types of chest screens are vibratory, gravity, and centrifugal. The material is then sent to wet silo.

(v) Digestion

From wet silo, the material is sent to digester. The digester is usually **10 meters in length** and **2 meters in diameter**. It is made of steel and wrought iron. This is the main unit of the process. The digestion process can be either **batch** or **continuous**. In our country **batch process is mostly used**.

As the raw material enters into the digester, steam is introduced at the bottom and a liquor containing sodium sulphite is injected simultaneously to cover the raw material. Sodium sulphite used is buffered with sodium carbonate or sodium hydroxide to maintain its **pH 7-9**.

The digester is closed carefully. It is revolved at **2.5 R.P.M.** and a temperature of **160-180°C** is maintained. The digester takes **45 minutes** to attain the desired temperature after which it gets switched off automatically and pressure is released.

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(vi) Blow Tank

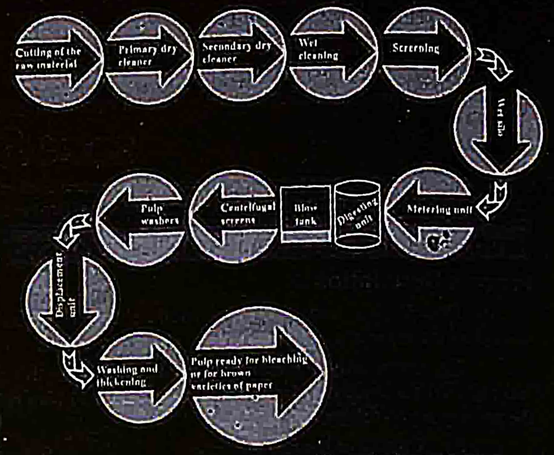
The cooked material from the digester is blown into a blow tank and then pumped to a centrifugal screen for the separation of cooked from uncooked materials.

(vii) Pulp Washing

The cooked material from the blow tank is washed thoroughly with water using 80 mesh sieve to remove the black liquor that would contaminate the pulp during subsequent processing steps. The pulp is washed with required amount of water to remove soluble lignin and coloured compounds. **Lignin** is an aromatic polymer and causes paper to become brittle. It is then thickened and finally stored in high-density storage tower.

(viii) Bleaching

The pulps obtained from chemical pulping are brown in colour and are unsuitable for printing and writing papers which require a bright white pulp. The colour of these pulps is mainly due to residual lignin. These pulps are then sent to bleaching unit.



Flow sheet diagram for neutral sulphite semi-chemical process

In Pakistan, bleaching is done with chlorine (Cl_2) or sodium hypochlorite (NaClO) and hydrogen peroxide (H_2O_2). After washing the unbleached pulp is sent to the chlorinator where chlorine **4–5 bar pressure** is injected from chlorine tank. The chlorine reacts with unbleached pulp at about 45°C for 45-60 minutes to give good results. The residual chlorine is neutralized with water which acts as antichlor. The correct dosage is important and calculated amount of chlorine is needed to achieve the required brightness. After chlorination, pulp is washed with hot water at 60°C and is then sent to the storage tank. Pulp is dried with hot air supply. After drying, the pulp is ready for manufacturing of paper.

(ix) Stock Preparation Plant

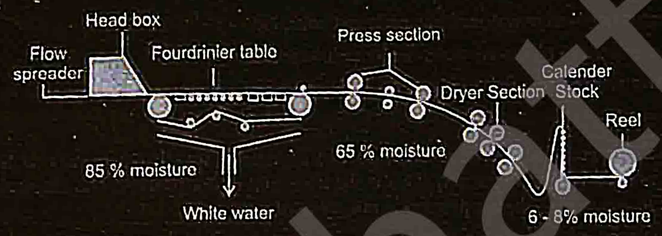
There are three important stages in the treatment of the pulp prior to its delivery to the paper making machine. The **first** is the dispersion of the pulp as a slurry in water, the **second** is the mechanical refining or beating of the fibres to develop appropriate physical and mechanical properties for the product being made and the **third** is the addition of chemical additives and recycled fibres from the waste paper plant. Wet end chemistry of paper start from here.

(x) Paper Making Machine

Commonly Fourdrinier machine is used for paper making. Its detail is given below.

(a) Flow Spreader

The flow of spreader takes the pulp and distribute it evenly across the machine from back to front. Consistency of the stock is below 1%.



Fourdrinier Paper making machine

(b) Head Box

The pressurized head box discharges a uniform jet of pulp suspension on a fabric, where special suction devices work for the removal of water.

(c) Fourdrinier Table

The endless, moving fourdrinier fabric forms the fibre into a continuous matted web while the fourdrinier table drains the water by suction forces.

(d) Press Section

The paper sheet is conveyed through a series of roll presses where additional water is removed and the web structure is consolidated. (i.e. the fibres are forced into intimate contact).

(e) Dryer Section

Wet sheet of paper so formed is dried in the dryer section of the machine with the help of rotary drum. Water is separated from the fibre either by gravity, by suction or by pressing and by heating.

(f) Calendar Stock

The sheet is calendared through a series of roll nips to reduce thickness and smooth the surface.

(g) Reel

The dried paper is wound in the form of a reel having final moisture of about 6-8%.

Q10a What are the common bleaching agents used in paper industry in Pakistan?

Common Bleaching Agents Used in Pakistan

In Pakistan, bleaching is done with

(i) Chlorine (Cl_2) (ii) Sodium hypochlorite (NaClO)

(iii) Hydrogen peroxide (H_2O_2)

Q10b What are the prospects of paper industry in Pakistan?

Paper Industry in Pakistan

Paper plays such an important role in the present day economic development that its consumption is taken as an index of a country's progress and prosperity. There was no pulp and paper industry in Pakistan at the time of independence in 1947. The country consumed about **25000 tons** of pulp and paper products per year and all of these were imported from abroad at a cost of **25 million rupees**. The start of the paper industry in our country was very slow because of various reasons amongst the major ones being the non-availability of suitable fibrous raw material.

Due to high prices of paper in Pakistan, it's per head consumption is among the lowest in the world. Paper consumption in Pakistan is around **5 kg per person per year.**

To make our country self-sufficient in this important commodity, we must utilize every source of raw material like non-woody and woody. Fortunately, Pakistan has enough source of non-woody material, which in future can meet the requirements of our pulp and paper industry. The efforts are being made to install more pulp and paper industries in the country.

At present there are more than **30 pulp and paper industries** in private as well as in public sectors, which are manufacturing pulp and paperboard.

KEY TERMS

1. Agriculture has been one of the oldest industry known to man. Since 5000 B.C. Chinese have been using animal manure in their fields.
2. Fertilizer is the natural or artificial substance containing the chemical elements that improve growth and productiveness of plants.
3. Natural fertilizers are materials derived from plants and animals whereas artificial fertilizers consist of manufactured material like urea, super phosphate and ammonium nitrate, etc.
4. Synthetic fertilizers are mainly used for making up the immediate deficiency of essential nutrient elements needed in relatively large amount.
5. The nutrients required in a very small amount for growth of plants are called micronutrients and the nutrients which are required in a very large amount are called macro-nutrients.
6. Urea and ammonium nitrate are the major nitrogeneous fertilizers whereas super phosphate and triple phosphate are important phosphatic fertilizers.
7. Cement is a very important building material which was first introduced in 1824 by an English mason Joseph Aspdin.

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8. Cement is the material obtained by burning an intimate mixture of calcarious and argillaceous materials at sufficiently high temperature to produce clinkers which are subsequently ground to a fine power. Wet process is generally used in the production of cement.
9. The use of cement for construction purposes is based on its property of setting to a hard mass when mixed with water.
10. Paper is a sheet material made up of a network of natural cellulosic fibers.
11. The neutral sulphite semi-chemical process is often used for the manufacturing of paper because of the advantages in the chemical recovery and pulp strength.
12. The prime objective of all pulp making steps is to separate fibres present in the straw from cementing material called lignin, which is natural binder.

SOLVED OBJECTIVE EXERCISE

Q1. Fill in the blanks.

(i) Fertilizers enhance the natural _____of the soil.
(ii) Micro-nutrients are required in quantity ranging from _____ per acre.
(iii) Ammonia contains _____ % nitrogen.
(iv) Manure is an _____ material used to fertilize land.
(v) Cement was first introduced by an English mason_____.
(vi) Phosphorus is required to stimulate_____ of plant.
(vii) In Pakistan, bleaching of pulp is carried out with_____
(viii) Cement is generally manufactured using _____ process.
(ix) The use of cement in the construction of building is based on its property of _____when its paste with water is allowed to stand for sometime.
(x) Lignin is an _____ polymer and causes paper to become brittle.

Answer Key.

(i)	Fertility	(ii)	6-200 g
(iii)	82%	(iv)	organic
(v)	Joseph Aspdin	(vi)	Early growth
(vii)	Chlorine dioxide or Sodium hypochlorite and hydrogen peroxide	(viii)	Wet
(ix)	Setting	(x)	Aromatic

Q2. Indicate True or false.

(i) Potassium fertilizers are especially used for tobacco and corn.
(ii) Ammonia is used in gaseous state while all other fertilizers are used in solid form.
(iii) In wet process for the manufacture of cement, grinding of raw material is done in the presence of water.
(iv) The total production of cement in Pakistan is 56,30,100 metric tons/annum.
(v) In neutral sulphite semi-chemical process, sodium sulphite is used buffered with sodium carbonate.
(vi) Lignin is an inorganic binder.
(vii) Paper consumption in Pakistan is around 5kg per person per year.
(viii) Urea contains 90% nitrogen.
(ix) The temperature of the digester in paper industry should be around 160-180° C.
(x) Potassium fertilizers increase the capability of plants to resist diseases.

Answer Key.

(i)	True	(ii)	False	(iii)	True	(iv)	False	(v)	True
(vi)	False	(vii)	True	(viii)	False	(ix)	True	(x)	True

Q3. Multiple choice questions. Encircle the correct answer.

(i) Which three element are needed for the healthy growth of plants.
(a) N,S,P (b) N,Ca,P (c) N,P,K (d) N,K,C

(ii) Which woody raw material is used for the manufacture of paper pulp.
(a) Cotton (b) Bagasse (c) Poplar (d) Rice straw

(iii) The nitrogen present in some fertilizers helps plants.
(a) To fight against diseases (b) To produce fat
(c) To undergo photosynthesis (d) To produce protein

(iv) Phosphorus helps the growth of.
(a) Root (b) Leave (c) Stem (d) Seed

(v) Micro-nutrients are required in quantity ranging from.
(a) 4–40g (b) 6–200g (c) 6–200kg (d) 4–40kg

(vi) During the manufacturing process of cement the temperature of the decomposition zone goes up to
(a) 600°C (b) 800°C (c) 1000°C (d) 1200°C

(vii) The word paper is derived from the name of which reedy plant.
(a) Rose (b) Sun flower (c) Papyrus (d) Water Hyacinth

(viii) Which is not a calcarious material.
(a) lime (b) clay (c) marble (d) marine shell

(ix) How many zones through which the charge passes in a rotary kiln.
(a) 4 (b) 3 (c) 2 (d) 5

(x) Ammonium nitrate fertilizers is not used for which crop.
(a) Cotton (b) Wheat (c) Sugar care (d) Paddy rice

Solved Exercise MCQs

Q.No.	Answer	Reason
(i)	(c) N, P, K	N = Nitrogen, P = Phosphorus, K = Potassium
(ii)	(c) Poplar	Cotton, bagasse and rice straw are non-woody raw materials.
(iii)	(d) To produce Protein	Nitrogen is main constituent of protein.
(iv)	(d) Seed	Phosphorus stimulates early growth and accelerates seed formation.
(v)	(d) 6 – 200g	Micro-nutrients are required in less amount.
(vi)	(b) 800°C	According to new text book in decomposition zone the temperature goes upto 900°C.
(vii)	(c) Papyrus	Papyrus grew along marshy delta of River Nile in Egypt.
(viii)	(b) Clay	Clay is argillaceous material.
(ix)	(a) 4	Each zone has a specific temperature.
(x)	(d) Paddy rice	Because microbial bacterial in flooded fields decompose ammonium nitrate to nitrogen.

Previous Board Questions

1. What are the principal methods of Chemical Pulping used for the production of paper? Which one is best and why?
2. Give four essential qualities of a good fertilizer.
3. Why NSSC Process in preferred over other processes in paper industry?
4. Name woody and non woody raw materials used for the production of pulp and paper.

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5. Explain reactions taking place in first 24 hours in setting of cement.
6. What is the function of argillaceous material in cement?
7. Describe digester in paper and pulp industry.
8. What are fertilizers? Name different nitrogenous fertilizers.
9. Name two phosphatic fertilizers. What they provide to plants or soil?
10. Discuss digestion process in the manufacturing of paper.
11. Name the macro-nutrient elements. How much they are required?
12. What is the composition of lime and silica in good cement?
13. What are the different zones in the rotary kiln? Give their temperature ranges.
14. Mention the importance of potassium fertilizers.
15. Name commonly use bleaching agents in paper manufacture?

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CHAPTER 16

ENVIRONMENTAL CHEMISTRY

Environmental Chemistry

"The branch of chemistry which deals with the chemicals and other pollutants in the environment is called environmental chemistry."

In this we study the sources, reactions, transportation of the chemicals and other toxic substances especially created by human activity in the environment and their adverse effects on human beings. This branch of chemistry is interrelated with all other branches of science, i.e. biology, physics, medicine, agriculture, public health and sanitary engineering, etc.

Components of the Environment

The environment consists of the following components.

(i) Atmosphere (ii) Hydrosphere (iii) Lithosphere (iv) Biosphere

(i) Atmosphere

The layer of gases which surrounds the earth is called atmosphere

- **Composition of Atmosphere**

Gas	%age	Gas	%age
N_2	78	CO_2	0.03
O_2	21	Ar	0.9

- Traces of H_2, O_3, CH_4, He, Ne, Kr and Xe are present in atmosphere.
- Traces amount of moisture or water vapours are also present in it.
- Its thickness is about 1000 km above the surface of the earth.
- Half of its mass is concentrated in the lower 5.6 km.
- The gases in the atmosphere absorb most of the cosmic rays and the major portion of the harmful electromagnetic radiation coming from the sun.
- The absorption of these harmful radiations protects the life on the earth.
- The gases present in the atmosphere are essential for sustaining life on earth *i.e.*, O_2 is required for breathing, CO_2 is required for plant photosynthesis, N_2 is used by nitrogen fixing bacteria.
- Water vapours are responsible for sustaining various forms of life on the earth.
- Atmosphere also maintains the heat balance of the earth.

(ii) Hydrosphere

The hydrosphere includes all water bodies, mainly i.e., oceans, rivers, streams, lakes, polar ice caps, glaciers and ground water reservoirs (water below earth surface).

1. Oceans contain 97% of earth's water but because of high salt contents this water cannot be used for human consumption.
2. The polar ice caps and glaciers consist of 2% of the earth's total water supply.
3. Only 1% of the total earth's water resources are available as fresh water *i.e.*, surface water; river, lake, stream and ground water. The fresh water is being used by agriculture (69%), industry (23%) and for domestic purpose (8%).

(iii) Lithosphere

"It consists of rigid rocky crust of earth and extends to the depth of 100 km."

The mantle and core are the heavy interior of the earth, making up most of the earth's mass.

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The 99.5% mass of the lithosphere is made of 11 elements, which are oxygen (~46.60%), Si (~27.72%), Al (8.13%), Fe (5.0%), Ca (3.63%), Na (2.83%), K (2.59%), Mg (2.09%), and Ti, H_2 and P (total less than 1%).

- The elements present in trace amounts (0.1 to 0.02%) are C, Mn, S, Ba, Cl, Cr, F, Zr, Ni, Sr and V.
- These elements mostly occur in the form of minerals.

(iv) Biosphere/Ecosphere

"Biosphere is the region of earth capable of supporting life."

It includes lower atmosphere, the oceans, rivers, lakes, soils and solid sediments that actively interchange materials with all types of living organisms *i.e.*, human beings, animals and plants.

Ecosystem: Ecosystem is a smaller unit of biosphere which consists of community of organisms and their interaction with environment e.g., animals, plants and microorganisms which lie in a definite zone and depend on the physical factors such as soil, water, and air.

Environment Pollutants

"Any substance in the environment which adversely affects the human health, quality of life and the natural functioning of ecosystem, is known as environmental pollutant." With continuous rapid growth in population, urbanization, industrialization and transportation, environmental pollution is spreading in almost every city of the world. The quantity of pollutants affecting the environments have increased rapidly in the last half-century and they have adversely affected human health and eco-system.

Types of Pollution

AIR POLLUTION

The atmosphere is polluted when harmful substances which damage the environment, human health and quality of life are mixed in it. The main sources of air pollution are:

Primary pollutants	Secondary pollutants
"The pollutants which are directly introduced into the environment are called primary pollutants."	"The pollutants which are produce in atmosphere through various reactions of primary pollutants are called secondary pollutants."
Examples: sulphur dioxide, sulphur trioxide, nitrogen oxides, carbon monoxide, hydrocarbons, ammonia, compounds of fluorine and radioactive materials.	**Examples:** sulphuric acid, nitrogen monoxide, carbonic acid, hydrofluoric acid peroxyacetyl-nitrate (PAN), ozone, aldehydes, ketones and peroxybenzol.

All the secondary pollutants are toxic and their concentration in the atmosphere must be controlled.

Sources of Primary Pollutants

Some sources of primary pollutants are given below:

1. Carbon Monoxide

- It is a colourless, odourless and highly toxic gas.
- It is three times lighter than air.
- It is soluble in water.

(a) Natural sources

Natural sources of carbon monoxide emission are volcanic eruption, natural gas emission and oxidation of methane in the atmosphere.

(b) Human Activities

Fuel burning in various types of transportation *i.e.*, motor vehicles, railways and aircraft is the major source (75%) of CO in the atmosphere. Other sources of carbon monoxide emission are forest fires, combustion of fossil fuel and agricultural products.

Carbon monoxide is also emitted from industries in which any type of fuel is burnt in air. These industries include iron and steel, petroleum, cement, brick kilns, paper and pulp, etc.

Incomplete combustion and dissociation of CO_2 at high temperature also produces CO.

- Carbon monoxide is highly poisonous gas.
- It causes suffocation if inhaled.
- It binds bloods haemoglobin more strongly than oxygen thus excluding oxygen from normal respiration.
- The CO poisoning can be reversed by giving high pressure oxygen.
- Exposure to high concentration of CO results in headache, fatigue, unconsciousness and eventually death (if such exposure is sustained for longer period).

2. Nitrogen Oxides (NO_x)

The gases, nitric oxide, NO and nitrogen dioxide, NO_2 are represented by NO_x.

(a) Natural Source

Bacterial actions produces NO_x mainly NO.

(b) Human Activities

Nitrogen oxides are generally produced by combustion of coal, oil, natural gas and gasoline. Both oxides result from the oxidation of nitrogenous compounds present in fossil fuel. The burning of fuel in the presence of air in internal combustion engine also produces NO.

$$N_2 + O_2 \xrightarrow{\text{high temperature}} 2NO$$

Nitrogen dioxide is produced when nitric oxide reacts with oxygen.

$$2NO + O_2 \longrightarrow 2NO_2$$

- The residence time of NO and NO_2 in the atmosphere are 4 and 3 days respectively.
- Due to photochemical reactions, NO_x are converted to HNO_3 which is carried down in either rain fall or as dust.

3. Sulphur Oxides (SO_2)

(a) Natural Source

On global scale most of sulphur dioxide is produced by volcanoes (67%) and by oxidation of sulphur containin gases produced by decomposition of organic matter.

(b) Human Activities

Air is polluted with SO_2 due to combustion of coal (containing 1-9% S), crude oil and other fossil fuel in pow plants and petroleum industry, etc.

$$S + O_2 \longrightarrow SO_2$$

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

- These gases (SO_2 and SO_3) because of their pungent odour are very irritant and suffocating.
- Through various reactions in the atmosphere they form sulphate aerosols.
- These aerosols cause severe respiratory troubles particularly among older people.
- Sulphur dioxide is the major source of acid deposition in the atmosphere.

4. Hydrocarbons

(a) Natural Source

Large quantities of hydrocarbons are emitted by different trees and plants in the atmosphere. Paddy fields produ a significant amount of methane in the atmosphere. Another natural source of methane is the anaerobic decomposition organic matter by bacteria in water sediments and in soils.

- Methane has a mean residence time of about 3 – 7 years in the atmosphere.

$$2CH_2O \xrightarrow{\text{Bacteria}} CO_2 + CH_4$$

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(b) **Human Activities**

Automobiles are the major source of hydrocarbons emission. In addition to this, petroleum, coal, wood, incinerators, refuse burning and solvent evaporator also contribute towards the emission of hydrocarbons into the atmosphere.

The Effects of Polluted Air on Environment

Q6. What is acid rain and how does it affect our environment?

Acid Rain

Acid rain which now-a-days is termed as acid deposition, was discovered by Angus Smith in Great Britain in the mid seventeenth century but this phenomenon gained importance as a serious environmental problem in 1950's. Initially it was referred to the precipitation which was more acidic than natural rain. Due to the presence of CO_2 in the atmosphere the natural rain itself forms carbonic acid:

$$CO_{2(g)} + H_2O_{(aq)} \longrightarrow H_2CO_{3(aq)}$$

The pH of unpolluted rain water should be 5.6. The rain water has pH less than 5 is considered truly acidic.

In the atmosphere SO_2 and NO_x are transformed by reactions with oxygen and water into H_2SO_4 and HNO_3 respectively. These acids get mixed with rain. The acid deposition includes both wet (rain, snow, fog) and dry acidic deposition.

$$SO_2 + \frac{1}{2}O_2 + H_2O \xrightarrow{\text{dissolution in smoke, Metal oxide}} H_2SO_4$$

In some countries due to release of HCl by volcanic eruption there is temporary acid rain.

Effect of Acid Rain on environment

(i) Acidification of the soil and rocks can leach metals like aluminium, mercury, lead and calcium and discharges them into water bodies. These heavy metals are accumulated in the fishes and are health hazards for humans and birds as they eat these fishes. The elevated concentration of aluminium is harmful for fish as it clogs the gills thus causing suffocation.

(ii) Acidification of the soil can also leach nutrients thus damaging leaves and plants and growth of forest.

(iii) It also damages building materials such as steel, paint, plastic, cement, masonry work and sculptural materials especially of marble and limestone.

Q7. What is smog? Explain the pollutants which are the main cause of photochemical smog?

Smog

"The word smog is a combination of smoke and fog" There are two types of smog.

(i) Reducing smog (ii) Oxidizing smog

(i) Reducing Smog

This smog contains high contents of SO_2. It is chemically reducing in nature and is known as reducing smog. The main cause of reducing smog is combustion of coal.

(ii) Oxidizing Smog (Photochemical Smog)

"The photochemical smog consists of higher concentrations of oxidants like ozone and is also termed as oxidizing smog."

- It is a yellowish brownish grey haze which is formed in the presence of water droplets and chemical reactions of pollutants in the air.
- It has unpleasant odour because of its gaseous components. The main reactants of photochemical smog are nitric oxide (NO) and unburnt hydrocarbons. Nitric oxide is oxidized to nitrogen dioxide within minutes to hours depending upon the concentration of pollutant gas.
- The yellow colour in photochemical smog is due to the presence of nitrogen dioxide.

Conditions for Smog Formation

The following conditions are required for the formation of smog.

1. There must be sufficient NO, hydrocarbons and volatile organic compounds (VOC) emitted by the vehicles
2. Sunlight, so that some of the chemical reactions may occur at a rapid rate.
3. The movement of air mass must be little so that reactions are not disturbed.

The overall result of photochemical smog in afternoon is the built up of oxidizing agents such as H_2O_2, HNO_3, peroxyacetyl nitrate (PAN) and ozone in the air.

- PAN is an eye irritant and is also toxic to plants.

Q8. Why is ozone layer depleting? What will happen when the concentration of ozone will be decreased?

Ozone

- Ozone is an allotrope of O_2.
- It has low boiling point and present in very small concentrations throughout the atmosphere.
- The amount of ozone in the atmosphere is expressed in **Dobson unit** (DU).
- The normal amount of overhead ozone is about 350 DU.

The ozone layer, 25 – 28 km high, in the stratosphere surrounds the globe and filters most of the harmful ultraviolet (UV) rays in the sunlight before they could reach on the earth. Therefore, if there is substantial reduction in the ozone layer the life on earth would be threatened. In 1980's a large hole in the ozone layer over Antarctic was discovered which represented a major environmental crisis.

Ozone is produced in most of the tropical regions by the photochemical reactions of oxygen, from where it is transported to polar regions. It acts as a pollutant and causes various health problems i.e., damages eyes and aggravates asthma, decreases the elasticity of lung tissues, coughing, chest discomfort, etc. It is harmful to the plants and other materials i.e., attacks rubber, reduces durability and appearance of paint and causes fabric dyes to fade. The amount of ozone is less in the regions closer to the equator.

Ozone Hole

The thickness of the ozone layer has been decreasing over Antarctic during the spring time since the mid 1970's. By the mid 1980's loss in ozone at some altitudes over Antarctica resulted in about 50% depletion of the total overhead amount. The region in which ozone depletes substantially in every year during Sep-Nov is now termed as "ozone hole".

The concentration of ozone in the stratosphere is being depleted through various chemical reactions not only above Antarctica but worldwide.

The stratosphere where the ozone layer exists in the atmosphere is approximately at 15 to 40 kilometer altitudes and is just above the troposphere which extends to an altitude of 0 – 15 kilometer from the earth. The temperature in troposphere decreases with the increasing altitude from 15 to -56°C, it is because the air near the earth is heated by radiation reemitted from the earth. Whereas the temperature in stratosphere increases with increase of altitude i.e., -56 to -2°C. The ozone is the main chemical species present in stratosphere which absorbs the ultraviolet radiation and increases the temperature in the upper part of the ozone layer.

Role of Chlorofluorocarbons (CFCs) in Destroying Ozone

Chlorofluorocarbons used as refrigerants in air conditioning and in aerosol sprays are inert in the troposphere but slowly diffuse into stratosphere, where they are subjected to ultraviolet radiation generating $Cl^\bullet$ free radicals. Chlorofluorocarbons (CFCs) play an effective role in removing O_3 in the stratosphere, due to following reactions.

$$CFCl_3 \longrightarrow CFCl_2^\bullet + Cl^\bullet$$

$$Cl^\bullet + O_3 \longrightarrow ClO^\bullet + O_2$$

$$ClO^\bullet + O \longrightarrow Cl^\bullet + O_2$$

- A single chloride free radical can destroy upto 100,000 ozone molecules.

WATER POLLUTION

Water is essential for life on earth. All living organisms contain water in them. To sustain life every human being drinks several litres of water daily. Marine or aquatic life is also impossible without water.

Surface and ground water which are vital resources of fresh water are vulnerable to contamination. The human activities such as livestock waste, landfills, agriculture, pesticides, oil leaks and spills, disposal of industrial effluents on

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open land, water bodies septic tanks, detergents, mining, petroleum and natural gas production may result in the contamination of the surface and ground waters.

1. Livestock Waste

Mostly the livestock waste is either being dumped on the open land or is discharged into sewage, canals or rivers. This practice pollutes the surface and ground water posing serious health problems to the population. Chemical and bacterial contents in livestock waste can contaminate surface and ground water causing such infectious diseases as dysentery (پیچش), typhoid (معیادی بخار) and hepatitis (ورم جگر).

2. Oil Spillage

Q.9 How is oil spillage affecting the marine life?

Petroleum or crude oil is a complex mixture of many compounds mainly hydrocarbons. The petroleum products are used as fuel, lubricant, for manufacturing petrochemicals, plastics, electrical appliances, synthetic rubber and detergents, etc. Sea water gets polluted by accidental oil spills and leakage from cargo oil tankers in sea, tanker trucks, pipelines leakage during off shore exploration and leakage of underground storage tanks. Many petroleum products are poisonous and pose serious health problems to human, animals and aquatic life. Hydrocarbons particularly **polycyclic aromatics** are known to be **carcinogenic** even at very low concentrations. The marine organisms are severally affected by soluble aromatic fractions of **oil (C–10 or less)**. The spilled oil damages the **marine life** often causing death. The light transmission through surface of water is affected by oily layer on it thus photosynthesis of the plants and dissolved oxygen in water is decreased.

3. Detergents

Q.10 How detergents are threat to aquatic animal life?

Detergents are excessively used in industries and household as cleaning agents. The amount of disposed detergents in waste water is increasing day-by-day. This waste water when discharged in rivers or sea, greatly affects the aquatic life, detergent contents of waste water mobilize the bound toxic ions of heavy metals such as Pb, Cd, and Hg from sediments into water.

4. Pesticides

Pests harm crops and transmit diseases both to human beings and animals. "Pesticides are the substances that can directly kill an unwanted organism or otherwise control by interfering with its reproduction process." The current ability to produce large amounts of food on relatively small amount of land has been made possible around the world by the use of pesticides. At present more than ten thousand different types of synthetic organic pesticides have been formulated. They are broadly classified into several principal types according to their general chemical nature. The most important and widely used pesticides are **insecticides** (which kill insects), **herbicides** (which kill undesired plants) and **fungicides** (which control the growth of fungus on the plant).

The use of various pesticides also helped in the eradication of diseases such as malaria, yellow fever (یرقان), bubonic plague (گلٹی دار طاعون) and sleeping sickness (ہر وقت نیند آنا).

Wide spread use of pesticides for getting greater crop yields if not properly checked and controlled has associated risks of contaminating the soil, plants and water. The drainage water from the agricultural land (where the pesticides are being used) mostly contains pesticides. Therefore if the use of any type of pesticide is not properly controlled it enters through various roots i.e., agricultural food products and drinking water into the food chain and thus pose serious health problems to both human beings and animals.

Organic chemicals in drinking water do not have any healthy effects on human or animal health.

1. Some organic chemicals may have no detrimental effects at low concentrations. But many compounds once thought safe, especially the synthetic organic chemicals, can have serious and substantial health risks, even at very low concentrations. At even **higher concentrations**, most of the compounds are tasteless and odourless.
2. It is now known that many of the light molecular weight chlorinated **hydrocarbons in drinking water** are **carcinogens** and they have no safe levels. That is they cannot be consumed through air, food, or water without the risk of adverse health effects.
3. When synthetic organic chemicals are **ingested through food** or drinking water, they can cause health problems. At high concentrations, they can cause nausea (متلی), dizziness tremors (بے ہوشی کے دورے), and blindness (اندھا پن). At lower concentrations, at which these compounds become tasteless and odourless, humans may develop skin eruptions or central nervous system impairment (اعصابی بگاڑ). At still lower concentrations when ingested over

months or years, the compounds can cause health problems. With human or animal carcinogens, there is often a long period of time between exposure and manifestation of the disease.

5. Industrial Waste Effluents

Q.13 Discuss industrial waste effluents?

The finished products in any chemical related manufacturing industries *i.e.*, **leather, tanneries, fertilizers, or refining, petrochemical, textiles, paper pulp and paper board, rubber products, agro-chemicals, leather goods,** etc. are always accompanied by some by-products and waste effluents. The waste products may be in the form of waste heat, smoke, solid or waste water effluents.

The industrial waste pollutants may contain organic chemicals including highly toxic synthetic organic compounds and heavy metals i.e., Pb, Cd, Cr, Hg, As, Sb etc, oils and greases, mineral acids, etc. The toxic organic compounds and heavy metals and metalloids results in contamination of both surface and ground water used for irrigation and potable water supply. This also causes irreversible degradation of the environment causing serious health problems for public and marine life.

It must be mentioned here that heavy metals such as Pb, Cd, Cr, As, Hg, etc. are highly toxic and do not have any safe limits; they have accumulation effects when ingested through food or water and cause various health problems like anaemia, kidney diseases, nervous disorder, high blood pressure etc.

6. Leather Tanneries

Many leather tanning units, varying from the cottage scale to big industrial units, are working in and around many big cities of Pakistan. They use big quantities of chromium (VI) salt for leather tanning. They are producing good variety of exportable leather but only some units have the facility of waste water treatment by reducing Cr (VI) into trivalent state followed by alkaline precipitation of $Cr(OH)_3$. The effluents are discharged onto the open land or put into the sewage system. These industries are the big source of chromium (VI) pollution in the environment. Chromium (VI) is highly toxic and is known to cause cancer.

Factors Affecting the Quality of Water

The terms dissolved oxygen, biochemical oxygen demand and chemical oxygen demand are frequently used in measuring the quality of water. These terms are described as follows:

(i) Dissolved oxygen (DO)
(ii) Biochemical Oxygen Demand (BOD)
(iii) Chemical Oxygen Demand (COD)

Quality of Water
DO ∝ purity of water
BOD ∝ 1/purity of water
COD ∝ 1/purity of water

(1) Dissolved oxygen (DO)

In water the most important oxidizing agent is dissolved molecular oxygen (O_2) the concentration of which ranges from 4-8 ppm. The organic matter is oxidized with the help of this dissolved oxygen in water. It is a parameter to determine the quality of water. The dissolved oxygen value less than 4 ppm indicates that water is polluted.

(2) Biochemical Oxygen Demand (BOD)

It is capacity of organic matter in natural water to consume oxygen within a period of five days. "The value of BOD is the amount of oxygen consumed as a result of biological oxidation of dissolved organic matter in the sample."

The oxidation reaction is catalyzed by microorganisms which are already present in the natural water. It is measured experimentally by calculating the concentration of oxygen at the beginning and at the end of five days period, in which a sealed water sample is maintained in the dark at constant temperature either at 20°C or 25°C.

(3) Chemical Oxygen Demand (COD)

"The organic content of water which consume oxygen during chemical oxidation is evaluated by its chemical oxygen demand."

The oxygen demand of water can be determined directly by treating it with dichromate ions $Cr_2O_7^{-2}$ which is a powerful oxidizing agent. The organic matter in water is oxidized while the remaining dichromate is determined by titremetrically.

Value of COD is a direct measure of chemically oxidizable matter in water. Higher values of COD will indicate more pollution.

PURIFICATION OF WATER

The surface or ground water is normally used for drinking and other domestic purposes. The quality of untreated surface or ground water varies largely from place to place.

"The water obtained from rivers, lakes, glaciers and oceans is called surface water."

Surface water has various contaminations in it and required some treatment before use. Water is purified by the following stages.

(1) Aeration

The quality of raw water is improved by aeration. In this process air is passed through the water.

(i) To remove the dissolved foul smell gases like H_2S, organo sulphur compounds and volatile organic compounds.

(ii) Some of the organic materials in the raw water which could be easily oxidized with air produce CO_2 in the aeration process. The remaining portions of organic material if necessary are removed by passing water over activated carbon.

(iii) Aeration process also oxidizes water soluble Fe^{2+} to Fe^{3+} which then forms insoluble $Fe(OH)_3$ and can be removed as solid.

(iv) Aeration also improves the oxygen level of raw water.

(2) Coagulation

The materials which are suspended or present in the colloidal form in raw water are removed by coagulation

- The coagulant such as aluminum sulphate or alum is added to the raw water, which causes the precipitation of suspended impurities. For example, aluminum hydroxide is precipitated when alum is added to water in alkaline medium i.e.

$$K_2SO_4.Al_2(SO_4)_3.24H_2O + 3Ca(OH)_2 \longrightarrow 3CaSO_4 + 2Al(OH)_3 + K_2SO_4 + 24H_2O$$

Many suspended particles get adsorbed on the surface of gelatinous aluminum hydroxide precipitate.

- Ferric salts are also commonly used as coagulants but they are difficult to handle because an insoluble ferric oxide is produced in the pH range from 3.0 to 13.0.
- The process of coagulation can remove more than 80% of the suspended solids in the raw water.
- The surface or ground water may also contain calcium and magnesium salts which make the water hard. The hard water is then appropriately treated to remove Ca^{2+} and Mg^{2+}.

(3) Water disinfertions by Chlorine

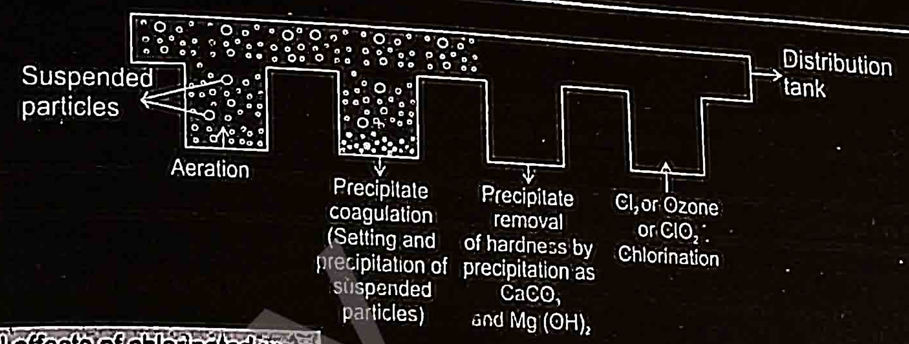
Chlorine is frequently used to disinfect water. Chlorine treatment is very effective in killing the pathogens that may cause serious water-borne diseases such as typhoid and cholera. Which have killed many thousands of people around the world.

The most commonly used disinfecting agent is hypochlorous acid HOCl. This neutral covalent compound kills microorganisms readily by passing through their cell membranes.

The hypochlorous acid is unstable thus it cannot be stored, it is therefore generated by either dissolving molecular chlorine gas or sodium and calcium hypochlorite in water, Disinfections by chlorines is inexpensive.

$$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^-$$

Generating HOCl from sodium or calcium hypochlorites avoids the transportation and use of chlorine cylinders.



Harmful effects of chlorinated water

Chlorinated water has also some harmful effects which are discussed below.

1. Hypochlorous acid or chlorine of water reacts with dissolved ammonia to form chloramines NH_2Cl, $NHCl_2$ and NCl_3 (nitrogen trichloride) which is a powerful eye irritant

$$NH_3 + 3HOCl \rightarrow NCl_3 + 3H_2O$$

The alkaline pH can prevent the formation of chloramines.

2. Chlorination of water containing organic materials also forms some organic compounds which are toxic. For example, if phenol is present in water then chlorinated phenols are formed which have offensive odour and taste and are toxic.

3. Chloroform ($CHCl_3$) is formed when hypochlorous acid reacts with organic matter (humic acid) dissolved in water.

- Chloroform is suspected liver carcinogen and also has negative reproduction and development effects in humans.
- The risk of bladder and rectal cancer increases by drinking chlorinated water.

To avoide the formation of toxic compounds with chlorine, ozone (O_3) or chlorine dioxide (ClO_2) is used for the disinfection of water.

SOLID WASTE MANAGEMENT

Solid Waste

The disposal of domestic refuse, commercial and industrial solid wastes or semisolid materials are studied under the title solid waste management. The domestic municipal solid waste mostly consists of papers, vegetables, plastics, wood, glass, rubber, leather, textile, metals and food wastes.

The disposal of domestic, commercial, industrial, agricultural, or municipal solid waste is called solid-waste management.

Methods of solid Waste Disposal

Following methods are usually used for the disposal of the solid waste.

1. Dumping of waste in sea or river
2. Landfill
3. Incineration
4. Recycling

1. Dumping of waste in sea or river

Water covers more than 70% of the earth and is valuable source for food and minerals. Sea and rivers have long been used for dumping waste of , industrial and municipal discharges such as acids, refinery wastes, pesticides waste, construction and demolition debris, explosives, domestic refuse, garbage and radioactive waste, etc. The dumping of waste materials in water has damaged the marine environment and caused health hazards to human beings.

2. Landfill

The municipal solid waste is mainly disposed off by dumping it in a landfill.

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The landfill is a large hole in the ground or even a bare piece of land. When the landfill becomes full with waste, it is covered by soil or clay.

The site of land is selected on a number of factors such as topography, location of the ground, water table, nature of the solid waste, type of soil and rock and location of disposal zone in the surface water and ground water flow system.

Q15. What are leachates?

Leachate

The ground water which seeps in the landfill and liquid from the waste itself all percholate through the refuse is called leachate.

The gases which are produced in landfills from the waste are methane, ammonia, hydrogen sulphide and nitrogen. The leachate contains volatile organic acids such as acetic acid and various fatty acids, bacteria, heavy metals and salts of common inorganic ions such as Ca^{2+}. The micropollutants present in municipal solid waste include common volatile organic compounds such as toluene and dichloromethane.

3. Incineration of the Muncipal Solid Waste

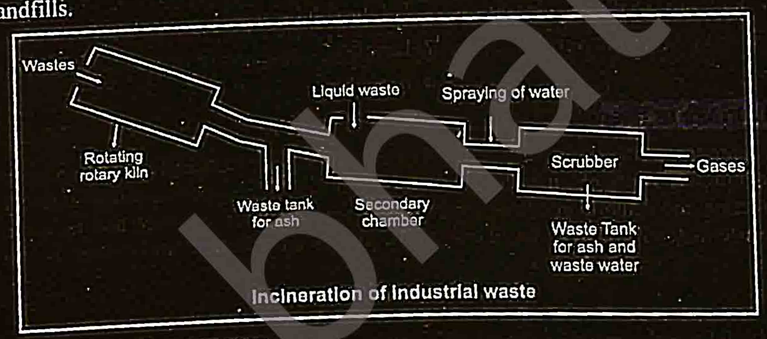
Incineration is a waste treatment process in which solid waste is burned at high temperatures ranging from 900 to 1000°C. The burning of the solid waste in the incinerator consumes all combustible materials leaving behind the non-combustible materials and the ash residues. The ash residues of the incinerator are disposed off on the land or landfills. The incineration may reduce the volume of the waste by two third. The combustible components of garbage such as paper, plastics and wood provide fuel for the fire. In incinerator, the heat of combustion may be used in producing steam which can run the turbine and electricity can be produced.

Treatment of Industrial Waste

The industrial and hazardous wastes are disposed off in landfill or the waste is first incinerated and the residual ash is then disposed off in the landfill. The landfill for the hazardous waste is monitored more regularly for the leakage of the leachate and its design is almost same as that of landfill for the muncipal solid waste, except it has more lining of clay and plastic so that the leachate does not contaminate soil and ground water around.

Incineration of industrial and Hazardous waste

A general process of high temperature incineration system consists of a rotary kiln which accepts all types of wastes including liquid, solid or sludge. The wastes are burned at temperatures between 650°C to 1100°C. Ash from the rotating chamber is collected at waste tank and the remaining liquid gaseous materials are passed to the secondary chamber. This chamber is non-rotating and hence the temperature range of 950°C to 1300°C is maintained. In this chamber organic molecules are completely destroyed. The gases produced are then cooled to 230°C by evaporating water spray. The cooled gases are then passed through scrubber system which eliminates the surviving particulates and acid forming components like CO_2, Ash residues and wastewater produced in the rotating and secondary chambers are disposed off in the landfills.



Incineration of industrial waste

Disadvantages of the incineration process

Although the volume of solid waste is reduced to a much lesser extent by burning it in incinerator, yet it has following disadvantages:

(i) It is not a clean process of the disposal of solid wastes, as it produces air pollution and also toxic ash.
(ii) Incineration of the solid waste is a significant source of dioxins which is a class of carcinogen compounds.
(iii) Smoke stacks from incineration may emit oxides of nitrogen and sulphur which lead to acid rain.
(iv) Heavy metals such as lead, cadmium, mercury, etc., may also be present in the leachate of the incinerators.

4. Recycling

In recycling some of the used or waste materials are not discarded after their initial use but are processed so that they can be used again. The purpose of recycling is to conserve sources such as raw material and energy. The volume of the waste is also much reduced by recycling of the materials. The most common domestic materials that are recycled are paper, plastic, glass and aluminium.

(i) Recycling of paper

The largest item which is recycled is newspaper and in its recycling process the release of chlorine or other bleaching acids and organic solvents is significantly less as compared to formation of these compounds during the processing of virgin newspaper. To improve the whiteness of the recycled newspaper it is blended with the virgin newspaper or sometimes treated with peroxides and hydrosulphites. In recycling process, the fibre of the newspaper becomes shorter so it can be recycled again and again for five times.

(ii) Recycling of Plastic

The recycling of plastics is done by reprocessing, depolymerization or transformation.

(a) In reprocessing the used plastics are re-melted and styrene which is used for the manufacturing of different products e.g., the original use of polystyrene is for the manufacturing of foam, packaging, cutlery, furniture etc. but after its reprocessing it is used mostly for the manufacturing of toys, trays etc.
(b) The depolymerization is a process in which the used plastics are converted back into their original components by a chemical or thermal process so that these can be subsequently polymerized again e.g., polyethylene terephthalate can be thermally depolymerized in the presence of a catalyst and heat into its original components.
(c) The transformation is a process in which used plastics are converted into low quality substances which are later used for the production of other materials e.g., cracking of polyethylene at high temperatures gives its monomers which are used for the manufacturing of lubricants.

KEY TERMS

1. Environmental chemistry is the branch of chemistry in which we study the sources, reactions, transportation and effects of the pollutants on the environment. The environment consists of our components.
2. The primary air pollutants are carbon monoxides, sulphur dioxide, sulphur trioxide, nitrogen oxides and hydrocarbons.
3. The acid rain is due to the oxides of sulphur and nitrogen whict get mixed with rain water in the presence of pollutants to form sulphuric and nitric acids. The acid rain affects the soil, water and sculptural materials.
4. The main cause of photochemical smog is the presence of oxidants such as nitrogen oxides in the atmospheres. The hydrocarbons also play a key role for smog formation.
5. The ozone is a protective layer in the stratosphere which absorbs harmful ultraviolet radiation of the sun and thus blocks them to reach on the earth.
6. Water which is an essential requirement for all the living beings on the earth is being polluted by livestock waste, oil spillage, detergents, pesticides and industrial wastes. The water pollution results in many infectious diseases such as dysentery, typhoid, hepatitis and in some cases also cancer.
7. The potable water is purified by aeration, coagulation and chlorination. Although chlorination has saved many thousand lives by killing viruses and bacteria, it also forms some chlorinated organic compounds in water which are toxic.
8. The domestic municipal solid waste consists of paper, plastic, vegetables, wood, glass, rubber, leather, textile, metals and food wastes. The waste whether domestic or industrial is managed by disposing it off in the landfills or it is initially incinerated and then the resulting ash is disposed off in the land or in landfills. The dumping of waste in ocean, sea and rivers have damaged the marine environment and caused health hazards for human beings.
9. In the recycling process instead of dumping the waste products i.e., paper, plastic, glass and aluminium, they are

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processed and made reusable. This process also reduces the volume of the waste.

SOLVED OBJECTIVE EXERCISE

Q1. Fill in the blanks.

(i) Only _____ of the total earth's water resources are available as fresh water.

(ii) _____ is a smaller unit of biosphere which consists of community of organisms and their interaction with environment.

(iii) Carbon monoxide is highly poisonous gas and causes suffocation if inhaled, it binds blood___ more strongly then oxygen thus excluding oxygen from normal respiration

(iv) The elevated concentration of ___ is harmful for fish as it clogs the gills thus causing suffocation.

(v) The ozone layer in ___surround the globe and filters most of the harmful rays in the sunlight before they could reach the earth.

(vi) The presence of ___ in livestock waste can contaminate surface and ground water causing various infectious diseases.

(vii) The substances which can directly kill the unwanted organisms are called ___.

(viii) _____ is frequently used to disinfect water.

(ix) Incineration is not a clean process because it produces air pollution and toxic ____.

(x) A process in which some of the used or the waste materials are not discarded after their initial use but are processed so that they can be used again is called ____.

Answer Key.

(i)	1%	(ii)	ecosystem
(iii)	Haemoglobin	(iv)	Aluminium
(v)	Stratosphere	(vi)	Chemical and bacterial contents
(vii)	Pesticides	(viii)	Chlorine
(ix)	Ash	(x)	Recycling

Q2. Indicate True or false.

(i) Half of the mass of the atmosphere is concentrated in lower 10 km.

(ii) The oceans cover approximately 71 percent of the earth.

(iii) The volcanoes produce 55% of SO_2.

(iv) The reducing smog is due to the presence of nitric oxide.

(v) Ozone is produced in the polar regions by the photochemical reaction of oxygen.

(vi) The temperature in the troposphere decreases with the increasing altitude from 15 to – 56° C.

(vii) Incineration is a waste treatment process in which solid waste is dumped in a land fill.

(viii) Acid rain is due to the presence of oxides of sulphur and nitrogen which get mixed with the rain water.

(ix) The heavy metals have a safe limit where they are not toxic.

(x) The reprocessing of the plastics is to convert back to their components by a chemical or thermal process so that these can be used again.

Answer Key.

(i)	False	(ii)	True	(iii)	False	(iv)	False	(v)	False
(vi)	True	(vii)	False	(viii)	True	(ix)	False	(x)	False

Q3. Multiple choice questions. Encircle the correct answer.

(i) The pH range of the acid rain is

(a) 7-6.5 (b) 6.5-6 (c) 6-5.6 (d) less than 5

(ii) Peroxyacetylnitrate (PAN) is an irritant to human beings and it affects.

(a) eyes (b) ears (c) stomach (d) nose

(iii) To avoid the formation of toxic compounds with chlorine which substance is used for disinfecting water.

(a) $KMnO_4$ (b) O_3 (c) Alums (d) Chloramines

(iv) A single chloride free radical can destroy how many ozone molecules

(a) 100 (b) 100000 (c) 10000 (d) 10

(v) Fungicides are the pesticides which

(a) control the growth of fungus (b) kill insects (c) kill plants (d) kill herbs

(vi) Ecosystem is a smaller unit of

(a) lithosphere (b) hydrosphere (c) atmosphere (d) biosphere

(vii) The main pollutant of leather tanneries in the waste water is due the salt of :

(a) lead (b) chromium (VI) (c) copper (d) chromium(III)

(viii) In purification of potable water the coagulant used is

(a) nickel sulphate (b) copper sulphate (c) barium sulphate (d) alum

(ix) The temperature in the non-rotating chamber in the incineration of industrial and hazardous waste process has a range.

(a) 900 to 1600 °C (b) 250 to 500°C (c) 950 to 1300°C (d) 500 to 900°C

(x) Newspaper can be recycled again and again by how many times.

(a) 2 (b) 3 (c) 4 (d) 5

Solved Exercise MCQs

Q. No	Answer	Reason
(i)	(d) Less than 5.	The rain having pH less than 5 contains more acidic contents due to which it is acidic.
(ii)	(a) eyes	PAN is an oxidizing agent and is irritant to eyes.
(iii)	(b) O_3	Chlorine produces harmful compounds like chloramines, $CHCl_3$ but O_3 does not form such compounds.
(iv)	(b) 100000	Chloride free radical is very reactive so it can destroy 100000 O_3 molecules.
(v)	(a) Control the growth of fungus	Fungicide → fungi (fungus) + cide (to kill)
(vi)	(d) Biosphere	Ecosystem consists of community of organisms and their interaction with environment while biosphere consists of all regions of earth capable of supporting life.
(vii)	(b) Chromium (VI)	Chromium (VI) is highly toxic and is carcinogenic.
(viii)	(d) alum	Alum causes the precipitation of suspended impurities.
(ix)	(c) 950° to 1300°C	In this chamber organic molecules are completely destroyed.
(x)	(d) 5	In recycling process, the fibre of the newspaper becomes shorter so it can be recycled again and again for five times.

Previous Board Questions

1. What is Leachate?
2. NO_x is a Pollutant, comment.
3. Write down the role of chlorofluoro carbons in destroying ozone.
4. What do you mean by the terms:
   (a) BOD (b) COD
5. What is hydrosphere? Give its composition.

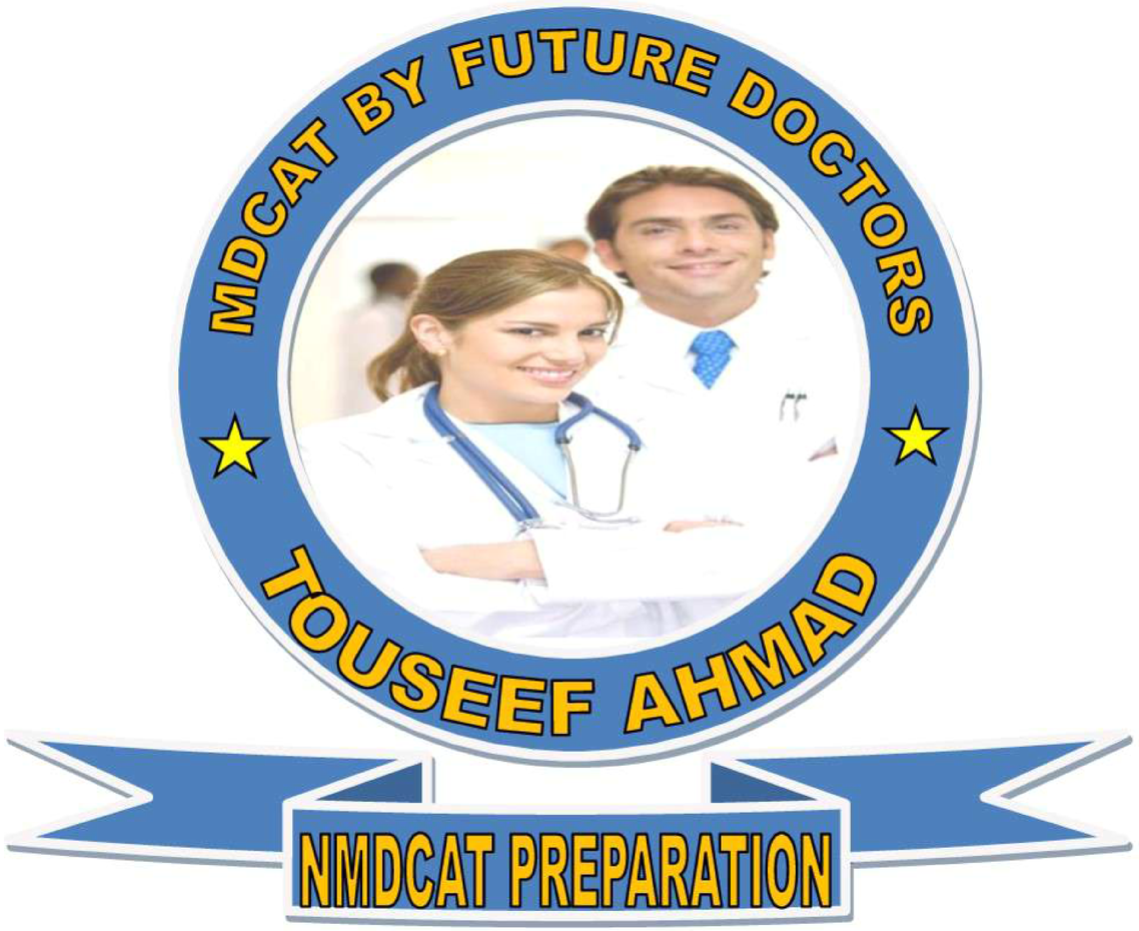
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6. Why is Ozone layer depleting?
7. Carbon monoxide is a main primary air pollutant. Give its effects on the human beings.
8. What is acid rain and how does it affect our environment?
9. What is the importance of dissolved oxygen in water?
10. What is lithosphere?
11. What is the unit used to measure the amount of ozone in the atmosphere and give its normal amount.
12. What are detergents? Give their types.
13. What is the purpose of ozone and what is the ozone hole?
14. What is meant by lithosphere and biosphere?

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